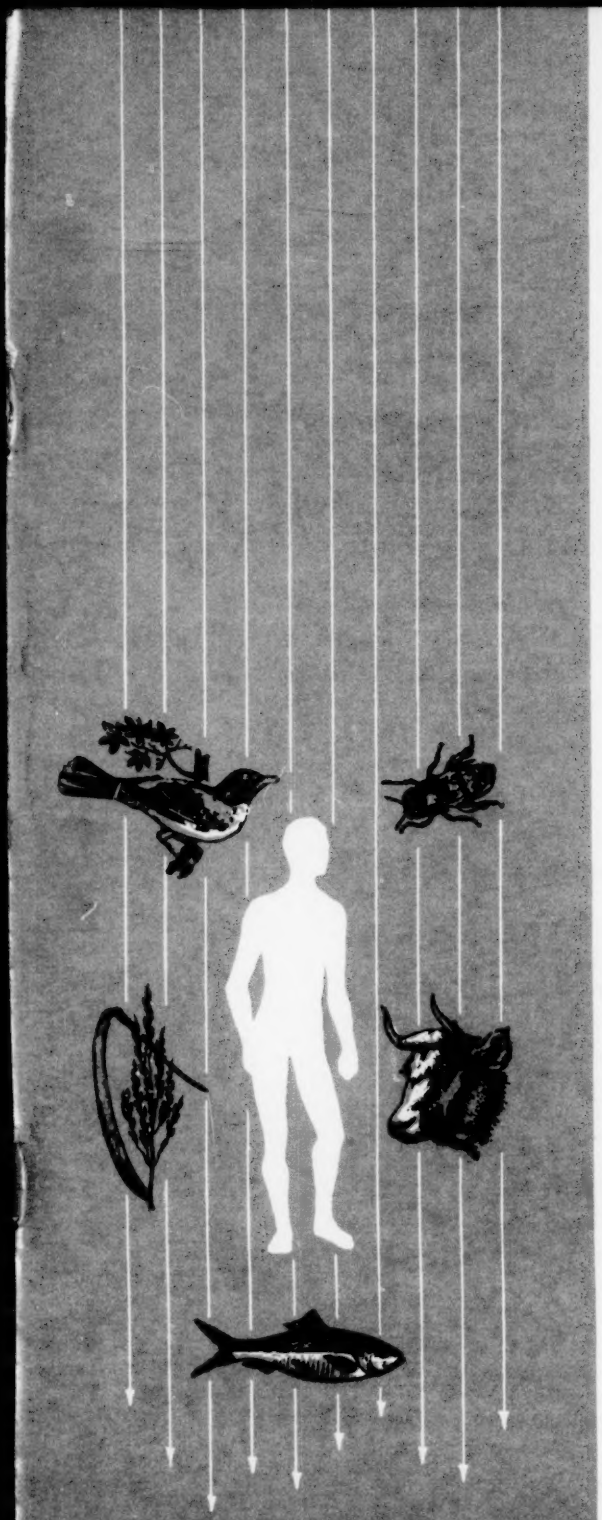

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# RESIDUES IN WATER

## *Analysis of Various Iowa Waters for Selected Pesticides: Atrazine, DDE, and Dieldrin—1974* [1,2]

John J. Richard, Gregor A. Junk, Michael J. Avery, Nancy L. Nehring, James S. Fritz, and Harry J. Svec

ABSTRACT

*Atrazine, DDE, and dieldrin were extracted and concentrated from various surface, subsurface, and finished waters using the macroreticular resin method. Organic components in the concentrates from these waters were separated by gas chromatography; the amounts of the three pesticides in the waters ranged from 0.5 to 42,000 parts per trillion by weight. Every major watershed in the State of Iowa revealed some degree of pesticide contamination and seasonal variations were consistent with agricultural runoff models. Atrazine concentrations were highest of the three pesticides, a symptom of its widespread use in the corn belt. DDE also appeared in substantial quantities, providing further evidence of the persistence of DDT and its metabolites. Water from several shallow wells and finished water from many water treatment plants were also contaminated. Current treatment processes do not effectively remove these pesticides.*

### *Introduction*

The present study was undertaken during the 1974 growing season to ascertain the degree and extent of contamination by dissolved pesticides of surface, subsurface, and finished drinking waters in the State of Iowa.

All major watersheds and several smaller ones were included in the survey of surface waters. During periods of heavy runoff, appreciable sediment was present but no attempt was made to measure pesticides sorbed in the suspended particles; thus pesticide content of surface waters quoted here represents only part of the total burden. For the subsurface and finished waters, quoted values accurately reflect the total pesticide burden because sediment was not a factor.

The survey of subsurface waters included both shallow- and deep-well systems within and outside the alluvial plains of contaminated rivers. The survey of finished water covered most of the major cities in the State including those which obtain their raw water from subsurface supplies.

Three pesticides were selected for monitoring: atrazine, DDE, and dieldrin. They are readily separated from interferences using gas chromatography (GC) and were present in amounts sufficient for quantification using electron-capture gas chromatography (EC/GC). These three pesticides were found in most of the water samples.

Atrazine is used in large amounts for weed control in cornfields and has appeared in runoff from small test plots of soil treated with atrazine (*1-7*). Aldrin and DDT have been used extensively in previous years and several investigators have found their metabolites, dieldrin and DDE, in Iowa rivers (*8-11*).

The most convenient method for isolating dissolved organic materials from the water prior to separation, identification, and quantification was by sorption on XAD-2 resin (*12-14*). The resin absorption method has two major advantages over solvent extraction: large sample volumes are possible without elaborate equipment, and the ratio of solvent used to amount of water sampled is very small.

### *Materials and Methods*

Petroleum ether (30°-60°C) and acetonitrile were pesticide quality. Diethyl ether was redistilled. Organic-free water was obtained by passing distilled water through a column containing XAD-2 resin and fresh activated charcoal. Organic-free sodium sulfate was obtained by heating anhydrous sodium sulfate at 400°C in a muffle furnace for 2 hours. The XAD-2 macroreticular resin received from Rohm and Haas in Philadelphia was prepared for column packing by slurrying in methanol and decanting to remove the fines and purifying by sequen-

[1] Supported in part by National Science Foundation Contract GP 33526X.

[2] Ames Laboratory, U.S. Atomic Energy Commission, and the Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa 50010.

tial Soxhlet extraction with methanol and acetonitrile (*12*). The purified resin was stored in a glass-stoppered bottle under methanol.

A Beckman GC-5 gas chromatograph equipped with a helium-dicharge EC detector was used for the gas chromatography. A 1.5 percent OV-17/1.95 percent QF-1 column was used for separating and quantifying the biocides. When large amounts of DDE were present, the dieldrin was quantified using a 5 percent OV-210 column.

The pesticide identifications were verified by comparing retention times using a 5 percent OV-210 column and a 10 percent DC-200 column. Additional confirmations were made using a Du Pont 21-490-1 gas chromatograph / mass spectrometer. When interference peaks on the EC gas chromatograms precluded accurate quantification of atrazine, samples were chromatographed on a 5 percent OV-1 column and mass fragmentography was employed to quantify the amount of atrazine present.

### GRAB SAMPLES

Grab samples of surface waters were collected in 4-liter amber reagent bottles. No velocity or depth integration was attempted to determine exact pesticide suspension. However, the sampling procedure was duplicated for each surface water supply. The sampling site for the three small streams, Skunk River, Indian Creek, and Fernald Drainage Ditch, was a single transverse position located at the centroid of flow halfway between the surface and the bottom. Water from sites 6, 7, 8, and 9 were analyzed in triplicate from various sampling sites and results varied by less than 1 percent. All other grab samples of surface waters were taken 6 inches below the surface. The collected water samples were allowed to settle overnight before extraction with the XAD-2 resin.

The apparatus used for extracting the pesticides is shown in Figure 1. The settled water sample was decanted into the 5-liter reservoir and passed through the resin by gravity flow at a rate of 25-50 ml/min. When the water level reached the upper glass wool plug sediment from the bottle was transferred to the reservoir using several rinses with organic-free water. After all the water had passed through the resin, the stopcock was closed, the reservoir was removed, and 15 ml diethyl ether was added to the resin. About 5 ml was allowed to flow through the resin and collect in a 60-ml separatory funnel. The stopcock was then closed for 15-30 minutes after which the remaining 10 ml ether was collected in the separatory funnel. This elution procedure was repeated with a second 15-ml portion of ether which was combined with the first. The water layer was drained from the separatory funnel and final traces of water were removed from the eluate by adding 10-15 ml petroleum ether and 2-3 g anhydrous sodium sulfate. The mixture was shaken approximately 30 seconds and the liquid extract was transferred quantitatively to a concentration flask. The extract was concentrated to 1 ml using the micro-distillation procedures described previously (*12*). A 1-5-$\mu$l aliquot of the concentrated sample was gas-chromatographed without further treatment.

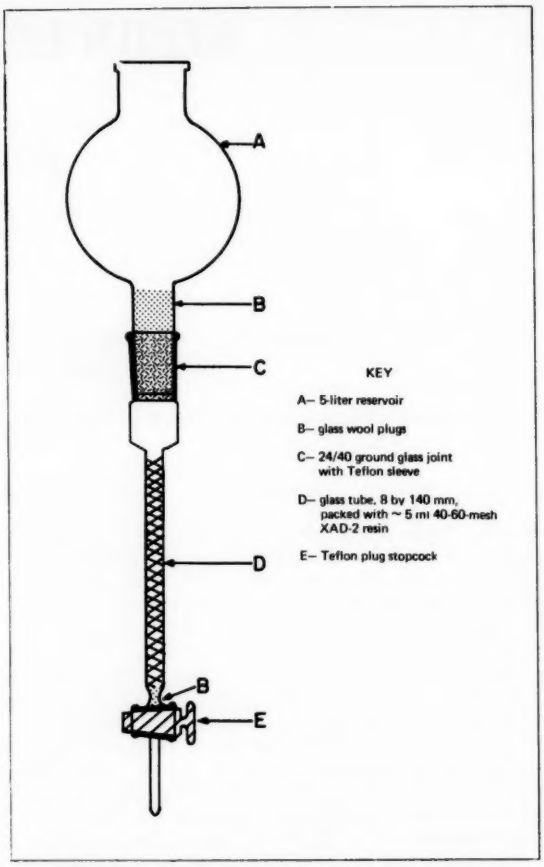


FIGURE 1. *Apparatus for extracting organic solutes from water*

This grab sampling procedure was also used for finished water samples unless low contamination was suspected or found in preliminary assays; in those cases an 8- to 16-liter water sample was used. An earlier study reported recoveries of atrazine, DDE, and dieldrin from water spiked at 20 parts per trillion (ppt) as 83, 81, and 93 percent, respectively, for the XAD-2 resin sorption procedure (*12*). In this study additional tests of the recovery of atrazine at the amounts reported here revealed values between 77 and 84 percent.

### COMPOSITE SAMPLES

The composite sampling procedure described below represents the average amount of pesticides present in the water over a 24-hour sampling period. The apparatus used is shown in Figure 2. Sampling was accom-

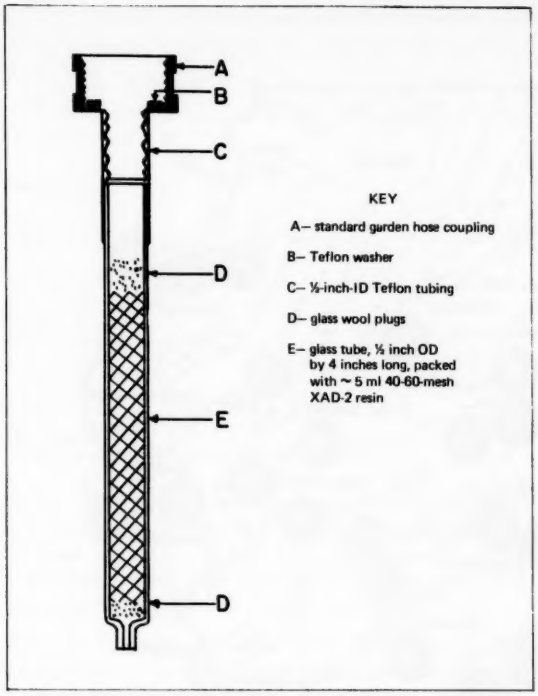


FIGURE 2. *Apparatus for extracting organic solutes from finished drinking water*

plished by attaching the standard garden hose coupling to a water faucet adjusted to deliver a flow of approximately 50 ml/min. After about 70 liters of water had been sampled during the 24-hour period, the XAD-2 column was removed from the coupling. Teflon sleeves were used to attach a reservoir and Teflon plug stopcocks to appropriate ends of the column. The column was then eluted with diethyl ether and the eluate was treated as described above for grab water samples. To insure that the capacity of the resin was not exceeded, tests were made using flows up to 150 ml/min and both longer and shorter sampling periods. All tests produced identical results which agreed with grab sample volumes of 8 liters. Either sampling procedure may be used for surface, subsurface, or finished waters, although grab sampling was used exclusively for all surface waters.

## *Results and Discussion*

Surface water samples were collected from rivers, reservoirs, and tributaries in major watersheds in the State of Iowa (Fig. 3). A small river, a creek, and a drainage ditch near Ames, Iowa, were sampled weekly and after each major rainfall. Des Moines and Raccoon Rivers and Rathbun and Redrock Reservoirs were sampled periodically throughout summer 1974. The Des Moines city finished water was sampled several times throughout spring and summer 1974. Finished waters from each of the other major cities in the State were sampled at least once during 1974. Atrazine had been found previously in many of these finished waters during a 1972 survey.

In general, pesticide contamination existed in all waters which originated from shallow wells in the alluvial plains of contaminated rivers and in all finished waters that originated from either surface waters or shallow wells. Amounts of the three pesticides present in the various waters are presented and discussed in separate sections.

### SURFACE WATER

Concentrations of atrazine, DDE, and dieldrin in water collected from the South Skunk River near Ames appear in Table 1. The first general rainfall in the river basin after corn planting in 1974 occurred June 8. That 3-inch rainfall was so intense that significant runoff and erosion occurred in the watershed upstream from the sampling point. Pesticide levels in the South Skunk River during the week immediately following the heavy rainfall correlate with discharge data for the river from the Geological Survey, U.S. Department of Interior.

TABLE 1. *Pesticide concentrations in South Skunk River near Ames, Iowa—1974*

| Sampling Date | Residues, ng/liter | | |
|---|---|---|---|
| | Atrazine | DDE | Dieldrin |
| 6/9 | 12,000 | 1,820 | 33 |
| 6/11 | 3,900 | 475 | 6 |
| 6/16 | 420 | 45 | 3 |
| 6/19 | 2,300 | 688 | 36 |
| 6/22 | 2,000 | 688 | 76 |
| 6/27 | 1,575 | 87 | 10 |
| 7/2 | 540 | 16 | 13 |
| 7/9 | 230 | 10 | 10 |
| 7/16 | 260 | 14 | 6 |
| 7/22 | 250 | 6 | 5 |
| 7/30 | 500 | 62 | 15 |
| 8/8 | 170 | 4 | 4 |
| 8/11 | 300 | 9 | 5 |
| 8/19 | 160 | 5 | 4 |
| 8/25 | 190 | 2 | 4 |
| 9/12 | 250 | 3 | 3 |
| 9/22 | < 100 | 3 | 3 |
| 10/13 | < 100 | 3 | 2 |

NOTE: Samples taken at site No. 1; see map, Figure 3.

Residues decreased with time following the June 8 rainfall. A similar pattern was established previously in studies of much smaller watersheds (*2-4*) and very small test plots (*1, 6*) where factors influencing pesticide loss were more closely controlled. The same pattern of pesticide loss after a single rainfall is evident for Indian Creek data in Table 2 and drainage ditch data in Table 3. However, no discharge data were available for those streams so no exact correlations between runoff and amount of pesticide in the water is possible.

Table 4 gives the concentration of atrazine, DDE, and dieldrin in Des Moines and Raccoon Rivers and Redrock and Rathbun Reservoirs. Values for the various

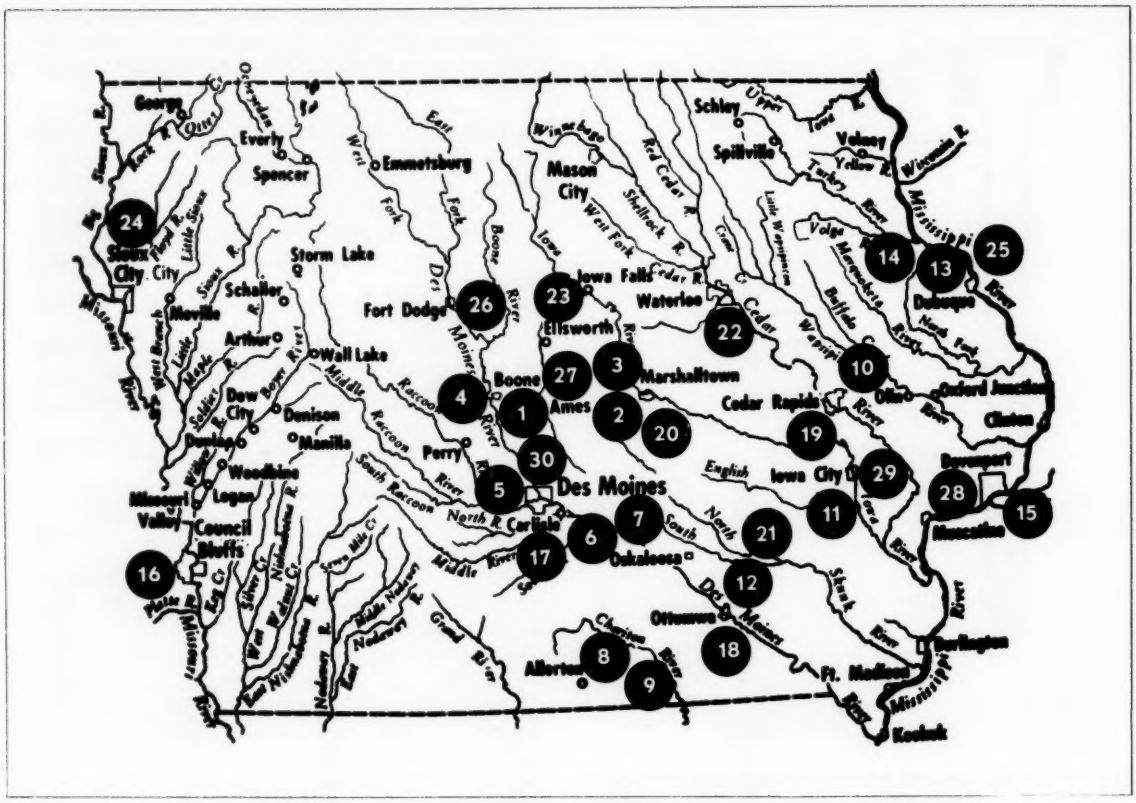


FIGURE 3. *Sites in Iowa watersheds sampled for selected pesticides, 1974*

TABLE 2. *Pesticide concentrations in east branch of Indian Creek near Fernald, Iowa—1974*

| Sampling Date | Residues, ng/liter | | |
|---|---|---|---|
| | Atrazine | DDE | Dieldrin |
| 6/9 | 42,000 | 3,920 | 25 |
| 6/11 | 3,400 | 600 | 7 |
| 6/16 | 870 | 80 | 4 |
| 6/19 | 2,000 | 910 | 30 |
| 6/22 | 2,400 | 435 | 71 |
| 6/27 | 1,075 | 100 | 17 |
| 7/2 | 510 | 6 | 9 |
| 7/9 | 255 | 6 | 8 |
| 7/16 | 210 | 8 | 7 |
| 7/22 | 285 | 4 | 6 |
| 7/30 | 880 | 34 | 24 |
| 8/8 | 163 | 6 | 8 |
| 8/11 | 225 | 5 | 6 |
| 8/19 | 300 | 4 | 4 |
| 8/25 | 300 | 2 | 4 |

NOTE: Samples taken at site No. 2; see map, Figure 3.

TABLE 3. *Pesticide concentrations in drainage ditch near Fernald, Iowa—1974*

| Sampling Date | Residues, ng/liter | | |
|---|---|---|---|
| | Atrazine | DDE | Dieldrin |
| 6/9 | 9,000 | 1,150 | 20 |
| 6/11 | 1,800 | 244 | 10 |
| 6/16 | 440 | 76 | 3 |
| 6/19 | 1,500 | 407 | 23 |
| 6/22 | 700 | 200 | 72 |
| 6/27 | 625 | 235 | 8 |
| 7/2 | 190 | 32 | 11 |
| 7/9 | 132 | 10 | 10 |
| 7/16 | 170 | 12 | 9 |
| 7/22 | 250 | 10 | 6 |
| 7/30 | 220 | 20 | 10 |
| 8/8 | 176 | 17 | 4 |
| 8/11 | 353 | 18 | 7 |
| 8/19 | 290 | 19 | 7 |
| 8/25 | 260 | 4 | 8 |

NOTE: Samples taken at site No. 3; see map, Figure 3.

TABLE 4. *Pesticide concentrations in surface water from Iowa sites sampled on several occasions—1974*

| Location | Sampling Site [1] | No. Dates Sampled | Period | Residues, ng/liter [2] | | |
|---|---|---|---|---|---|---|
| | | | | Atrazine | DDE | Dieldrin |
| Des Moines River Boone | 4 | 7 | 5/21-7/25 | 211(50-800) | 68(1-248) | 7(2-14) |
| Raccoon River Van Meter | 5 | 7 | 5/30-7/25 | 814(120-3300) | 59(2-250) | 7(1-12) |
| Red Rock Reservoir ~ 10 mi. upstream from dam | 6 | 6 | 5/19-7/25 | 813(60-2500) | 131(1-373) | 11(3-21) |
| Red Rock Reservoir dam site | 7 | 12 | 5/21-9/12 | 921(100-1900) | 212(8-350) | 18(5-36) |
| Rathbun Reservoir ~ 10 mi. upstream from dam | 8 | 5 | 4/21-6/25 | 4094(207-9400) | 420(5-1121) | 9(3-22) |
| Rathbun Reservoir dam site | 9 | 10 | 4/23-9/22 | 1285(165-3750) | 92(7-325) | 3(2-6) |

[1] See map, Figure 3.
[2] Figures in parentheses represent ranges.

periods correspond roughly with those in Tables 1-3 in that the concentrations are highest in the spring and decrease gradually during the growing season. This observation agrees with pesticide runoff concepts (*15*) and patterns observed for small watersheds (*3-6*).

Table 5 gives the values obtained for single samples collected at various times from rivers representing other major watersheds of the State; sampling was not coincident with rainfall. These random samples demonstrate the extent of pesticide contamination. That the biocide contamination is not a problem unique to areas adjacent to midwestern agricultural land is attested by results of analyses of water from the Mississippi River at New Orleans (Table 5).

TABLE 5. *Pesticide concentrations in surface water from Iowa and Louisiana sites sampled on one occasion, 1974*

| Location | Sampling Site [1] | Sampling Date | Residue, ng/liter | | |
|---|---|---|---|---|---|
| | | | Atrazine | DDE | Dieldrin |
| Cedar River Cedar Rapids, Iowa | 10 | 6/24 | 6,350 | 480 | 42 |
| Iowa River Iowa City, Iowa | 11 | 6/24 | 3,000 | 350 | 22 |
| Skunk River Oskaloosa, Iowa | 12 | 7/29 | 50 | 7 | 1 |
| Mississippi River McGregor, Iowa | 13 | 8/12 | 100 | 2 | <1 |
| Gremore Lake McGregor, Iowa | 14 | 8/12 | 190 | 4 | <1 |
| Mississippi River Davenport, Iowa | 15 | 7/30 | 331 | <0.5 | <0.5 |
| Mississippi River New Orleans, La. | | 7/30 | 1,200 | 48 | 7 |
| Missouri River Council Bluffs, Iowa | 16 | 8/15 | 80 | 0.5 | 0.6 |
| Farm Pond southern Iowa | 17 | 7/1 | 900 | 20 | 46 |
| Des Moines River Ottumwa, Iowa | 18 | 7/29 | 368 | 74 | 3 |

[1] See map, Figure 3.

It is not legitimate to compare amounts of contamination in various watersheds because of numerous variables such as time of sampling, climatic history, soil type, sediment load, and time of pesticide application that influence contamination of a river at any given time (*1, 15*).

### FINISHED WATER

The amounts of atrazine, DDE, and dieldrin in finished water samples from cities using wells as their source of raw water are given in Table 6. Water was contaminated

TABLE 6. *Pesticide concentrations in finished waters of Iowa cities which use well systems as raw water source—1974*

| Location | Sampling Site [1] | Sampling Date | Residue, ng/liter | | |
|---|---|---|---|---|---|
| | | | Atrazine | DDE | Dieldrin |
| Cedar Rapids [2] | 19 | 7/30 | 483 | 28 | 0 |
| Marshalltown [2] | 20 | 6/24 | 60 | 0 | 0 |
| Oskaloosa [2] | 21 | 7/29 | 14 | <0.5 | <0.5 |
| Waterloo [2] | 22 | 8/10 | 4 | <0.5 | <0.5 |
| Iowa Falls | 23 | 8/8 | <1 | <0.5 | <0.5 |
| Sioux City | 24 | 8/8 | <1 | <0.5 | <0.5 |
| Dubuque [2] | 25 | 7/4 | 0 | 0 | 0 |
| Fort Dodge | 26 | 8/8 | 0 | <0.5 | 0 |
| Ames | 27 | 6/19 | 0 | <0.5 | 0 |

[1] See map, Figure 3.
[2] Atrazine detected in 1972 survey.

in Cedar Rapids, Marshalltown, Oskaloosa, and Waterloo, cities which use shallow wells in the alluvial plains of the contaminated rivers. Sioux City, Dubuque, Fort Dodge, and Ames use well systems outside the alluvial plain of a contaminated stream; their water showed little or no biocide contamination.

Table 7 gives values obtained for finished waters collected from cities using surface water as their raw water source. Davenport filters Mississippi River water through granular activated carbon in its water purification scheme. The efficiency of activated carbon filtration for removing the pesticide contamination was tested by

TABLE 7. *Pesticide concentrations in finished waters of Iowa cities which use surface waters as raw water source—1974*

| Location [1] | Sampling Site [2] | Sampling Date | Residue, ng/liter | | |
|---|---|---|---|---|---|
| | | | Atrazine | DDE | Dieldrin |
| Davenport | 28 | 7/30 | 405 | 5 | 2 |
| Iowa City | 29 | 7/30 | 200 | 3 | 5 |
| Des Moines | 30 | 7/29 | 29 | 2 | 0.4 |

[1] Atrazine detected in 1972 survey at all three locations.
[2] See map, Figure 3.

monitoring biocides in raw water and in water which had passed through the carbon filter bed. Raw river water contained 331, $< 0.5$, and $< 0.5$ ppt atrazine, DDE, and dieldrin, respectively.

Corresponding residues in carbon-filtered water collected the same day were 469, 2, and 1 ppt. This increase in amounts of pesticides after carbon filtration agrees with findings by the U.S. Environmental Protection Agency (EPA) in 1973 (*16*). After monitoring the Davenport activated carbon bed, EPA officials concluded that occasionally the activated carbon treatment may add certain organic chemicals to the water depending upon the history of the activated carbon beds. Experience indicates, however, that odor and taste are removed by activated carbon beds long after they have apparently lost the capacity to remove other organic contaminants.

Des Moines obtains approximately 40 percent of its raw water directly from the Raccoon River and approximately 60 percent from an infiltration gallery that parallels the river for several miles. The amounts of the pesticides in water samples from the Raccoon River, the infiltration gallery, a mixture of the two, and the finished water are given in Table 8. All phases were

TABLE 8. *Pesticide concentrations in Des Moines, Iowa, water supply, raw and finished—1974*

| Source [1] | Date | Residues, ng/liter | | |
|---|---|---|---|---|
| | | Atrazine | DDE | Dieldrin |
| Raccoon River | 7/29 | 25 | 6 | 2 |
| Infiltration Gallery | 7/29 | 82 | 5 | 0.5 |
| Prefilter | 7/29 | 47 | 4 | 0.5 |
| Finished Water | 7/29 | 29 | 2 | 0.4 |
| Finished Water [2] | 8/1 | 60 | 2 | 1 |
| Finished Water [3] | 8/1 | 71 | 2 | 2 |

[1] Sampling sites 5 and 30; see map, Figure 3.
[2] 60-liter composite sample
[3] 16-liter grab sample

sampled the same day and the finished water was sampled again 3 days later. Exact comparisons of finished and raw water are not valid because of uncontrolled mixing which occurs in a large water plant and its distribution system. However, average values over a period of time for finished and raw water should be a valid indicator of the relative purities. For this reason samples of finished water from Des Moines were taken from June 1 to July 25, 1974. Average values for atrazine, DDE, and dieldrin were 515, 21, and 3 ppt, respectively. For approximately the same sampling period, average values of the three biocides in raw water from the Raccoon River were 814, 59, and 7 ppt. These results strongly suggest that current treatment processes do not significantly reduce pesticide contamination.

## *Conclusions*

The pesticides atrazine, DDE, and dieldrin were found in most of the water samples tested. Atrazine concentrations were highest of the three pesticides monitored, which is not surprising; atrazine is used widely on corn, a major product of Iowa, and has relatively high water solubility, 33 ppm. The substantial concentrations of DDE found provide additional evidence of the great persistence of DDT and its metabolites.

Water treatment plants are not removing substantial amounts of pesticides from raw water. Even filtration through activated carbon beds, as employed by one modern treatment plant in this study, is ineffective.

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# RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

## *Mirex Residues in Nontarget Organisms after Application of Experimental Baits for Fire Ant Control, Southwest Georgia—1971-72*

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### ABSTRACT

*Mirex, the only compound approved for control of the red imported fire ant* (Solenopsis invicta) *and the black imported fire ant* (Solenopsis richteri), *is normally applied at a rate of 1.40 kg/ha. (1.25 lb/acre). Influenced by recent studies showing that low levels of mirex are toxic to certain nontarget organisms, particularly estuarine species, authors report here on a monitoring study of mirex in three large treatment areas of southwest Georgia. Four formulations of bait were applied aerially in 1971-72. Low-level residues were observed in small terrestrial vertebrates and invertebrates and in fresh-water inhabitants. Levels detected were about the same for all baits. Maximum residues were detected 1-3 months after treatment and gradually declined to low levels of 0.02-1.16 ppm 1 year after treatment.*


### *Introduction*

The chlorinated hydrocarbon insecticide mirex is the only compound approved for control of the red imported fire ant, *Solenopsis invicta,* and the black imported fire ant, *S. richteri.* The insecticide, formulated at a concentration of 0.3 percent in a corncob grit/soybean oil bait, is normally applied at a rate of 1.40 kg/ha. (1.25 lb/acre).

Initially, residues were not considered to be a problem because of the very small quantities of mirex used and its low mammalian toxicity (*1*). However, recent laboratory studies have shown that low levels of mirex are toxic to certain nontarget organisms, particularly estuarine species (*2-4*), demonstrating the need for thorough monitoring of mirex residues in nontarget organisms following mirex bait applications. Several studies have been conducted on birds, other large terrestrial vertebrates, and aquatic and estuarine organisms (*5-12*), but very little work has focused on small terrestrial vertebrates and invertebrates or on fresh-water inhabitants.

The present paper reports the results of a monitoring study of mirex in three large treatment areas in southwest Georgia in 1971-72 following applications of a standard bait formulation and of three experimental formulations.

### *Methods and Procedures*

#### SAMPLE AREAS

Two experimental test sites were selected within each of three larger treatment blocks in Tift, Turner, and Worth Counties in southwest Georgia.

#### APPLICATION OF MIREX

Baits used in this study were formulated by Allied Chemical Corporation according to the procedures of Banks et al. (*13*). Four formulations of bait (Table 1) were applied in a series of three treatments (Table 2). Baits were dispersed from an altitude of 700 feet by multi-engine commercial aircraft under the supervision of personnel of the Plant Protection Division, Agricul-

TABLE 1. *Components of mirex bait applied for fire ant control, Georgia—1971-72*

| Formulation | Components of Bait, % log weight | | | |
|---|---|---|---|---|
| | Mirex | Soybean Oil | Corncob Grits | Latex Coating |
| A | 0.3 | 14.7 | 85.0 | NA |
| B | 0.15 | 14.85 | 85.0 | NA |
| C | 0.15 | 18.85 | 71.0 | 10.0 |
| D | 0.10 | 18.9 | 71.0 | 10.0 |

NOTE: Treatments A and B represent standard proportions of mirex, 0.3 percent and 0.15 percent. Treatments C and D were latex coated.


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TABLE 2. *Application patterns of mirex bait in three Georgia counties, 1971-72*

| Date | County | Formulation: Mirex, % | Area Treated | Bulk Rate [1] |
|---|---|---|---|---|
| Spring 71 | Turner | 0.3 (standard) | 25,369 ha. (62,640 acres) | 1.40 kg/ha. (1.25 lb/acre) |
| | | 0.15 (standard) | 12,685 ha. (31,390 acres) | 1.40 kg/ha. (1.25 lb/acre) |
| Spring 71 | Tift | 0.15 (latex coated) | 12,150 ha. (30,000 acres) | 1.12 kg/ha. (1.0 lb/acre) |
| | | 0.10 (latex coated) | 14,783 ha. (36,500 acres) | 1.12 kg/ha. (1.0 lb/acre) |
| Fall 71 | Worth | 0.10 (latex coated) | 40,500 ha. (100,000 acres) | 1.12 kg/ha. (1.0 lb/acre) |
| | | 0.3 (standard) | 40,500 ha. (100,000 acres) | 1.40 kg/ha. (1.25 lb/acre) |

[1] Numbers in parentheses show amount of actual toxicant, i.e., mirex, applied to each hectare.

tural Research Service, U.S. Department of Agriculture (USDA), (now a part of Animal and Plant Health Inspection Service, USDA). All aircraft operated under an electronic guidance system (*14*) and were equipped with auger-fed dispersal systems mounted within the wings of the aircraft.

### TREATMENT AND SAMPLING SCHEDULE

Dates of bait application and sample collection were as follows:

Turner County
- Pretreatment samples: May 24-28, 1971
- Baits applied: May 28
- 7-day posttreatment samples: May 31-June 4
- 1-month posttreatment samples: June 21-25
- 3-month posttreatment samples: August 23-26

Tift County
- Pretreatment samples: May 17-21, 1971
- Baits applied: May 25-June 2
- 7-day posttreatment samples: June 14-18
- 1-month posttreatment samples: July 6-9
- 3-month posttreatment samples: September 13-16

Worth County
- Pretreatment samples: September 28-October 5, 1971
- Baits applied: October 5-12
- 1-month posttreatment samples: November 8-12
- 6-month posttreatment samples: April 10-14, 1972
- 1-year posttreatment samples: September 1-8

### SAMPLE COLLECTION

Twenty pitfall traps for the collection of invertebrates and small vertebrates (*15*) were placed at sites which had been established randomly in each treatment area. Turner, Tift, and Worth Counties contained 5, 4, and 7 such trap sites, respectively. Hand collections were used to supplement pitfall collections whenever possible. Scientific and common names of species selected appear in Table 3.

Aquatic vertebrates were collected by hand and by seining from farm ponds located in each test area. The areas in Tift County treated with standard 0.15 percent and 0.3 percent baits contained two and one such ponds, respectively; the areas in Turner County treated with latex-coated 0.15 percent and 0.1 percent baits contained four and five collection ponds, respectively. Each of the Worth County test areas contained two collection ponds.

The pretreatment samples from Tift and Turner County and the 7-day posttreatment samples from Turner County were collected in 70 percent isopropanol as described by Markin et al. (*9*). However, authors found that isopropanol leached mirex from trapped specimens and thus distorted the values for mirex residues (*16*); therefore these samples were discarded. Subsequently,

TABLE 3. *Invertebrates and small vertebrates analyzed for mirex residues, Georgia—1971-72*

| Scientific Name | Common Name |
|---|---|
| **Insects** | |
| *Pictonemobius ambitiosus* | Ground cricket |
| *Neonemobius* near *mormonius* | Ground cricket |
| Subfamily Neombinae | Immature ground crickets |
| *Gryllus rubens* | Southern field cricket |
| *Gryllus firmus* | Sand cricket |
| *Gryllus fultoni* | Southern wood cricket |
| *Miogryllus verticalis* | Stripe-headed cricket |
| *Scapteriscus acletus* | Southern mole cricket |
| *Scapteriscus vicinus* | Changa |
| *Gryllotalpa hexadactyla* | Northern mole cricket |
| *Ceuthophilus* spp. | Camel crickets |
| *Parcoblatta* spp. | Wood cockroaches |
| *Cariblatta lutea* | Small yellow cockroach |
| *Chorisoneura texensis* | Small yellow Texas cockroach |
| *Ichnoptera deropeltiformis* | Dark wood cockroach |
| *Labidura riparia* | Riparian earwig |
| *Euborellia annulipes* | Ringlegged earwig |
| *Prosapia bicincta* | Twolined spittlebug |
| **Spiders** | |
| *Latrodectus mactans* | Black widow spider |
| **Isopods** | |
| *Armadillidium vulgare* | Pillbug |
| **Worms** | |
| | (Mixed unidentified earthworms) |
| **Mammals** | |
| *Cryptotis parva* | Least shrew |
| **Reptiles** | |
| *Cnemidophorus sexlineatus* | Sixlined racerunner |
| *Scincella laterale* | Brown skink |
| *Eumeces laticeps* | Greater fivelined skink |
| *Coluber constrictor priapus* | Southern black snake |
| *Natris sipedon fasciata* | Banded water snake |
| **Amphibians** | |
| *Rana sphenocephala* | Leopard frog |
| *Rana catesbeiana* | Bull frog |
| *Gastrophyryne carolinensis* | Narrow-mouth toad |
| *Bufo terrestris* | Southern toad |
| *Bufo quercicus* | Oak toad |
| *Acris gryllus* | Cricket frog |
| *Pseudoacris ornata* | Ornate chorus frog |
| **Fish** | |
| *Gambusia affinis* | Mosquito fish |
| *Lepomis macrochirus* | Bluegill |
| *Lepomis cyanellus* | Green sunfish |
| *Lepomis marginatus* | Dollar sunfish |
| *Fundulus lineolatus* | Lined topminnow |
| *Notemigonus crysoleucas* | Golden shiner |
| *Micropterus salmoides* | Largemouth bass |

technical crystals of chlorpyrifos were used in small open glass jars as the killing agent for specimens from pitfall traps.

The pitfall traps were checked everyday or every other day during each sampling period. During each collection period the contents of the 20 traps at each site were combined into one glass jar and quick-frozen in the field with dry ice. Aquatic vertebrates were wrapped in aluminum foil and frozen in the same manner. In the laboratory, all samples from a given treatment area and a single collection period were pooled into one composite. The pooled samples were separated by species and delivered to the Pesticide Research Laboratory, University of Florida, for analysis.

Species were selected to represent a cross-sectional sample of the food web. No pitfall or pond samples were collected within a half-mile of the boundaries of the treatment areas, in order to reduce the chance of contamination by other baits or by movement of animals. The limited widths of the treated areas precluded sampling of birds and larger mammals.

### *Analytical Procedures*

#### EXTRACTION

Samples dried in air to remove surface moisture, condensate, were weighed and then blended in at least 4 ml acetone per gram of sample at high speed for 4 minutes. The extract was filtered through a Buchner funnel, rinsed with fresh solvent, and transferred to a Kuderna-Danish concentrator. The acetone was partly evaporated on a steam bath, and *n*-hexane was added to the concentrator. The evaporation continued until the volume of hexane was reduced substantially. This procedure essentially removed all the acetone. The hexane was then concentrated to a known volume before cleanup.

#### CLEANUP

The extract, now in hexane, was cleaned by using florisil column chromatography. Three g of 60/100 mesh PR grade florisil was placed in 1-cm-ID glass columns fitted with a fritted glass disk. The florisil was topped with 2-3 cm anhydrous sodium sulfate and placed in a 150°C oven for at least 3 hours. Then the columns were prewashed with 50 ml hexane, and the washings were discarded. The extract, representing up to 1 g of sample, was placed on the column, and the mirex was eluted with 20 ml hexane. The hexane eluate was concentrated to 1.0 ml before gas chromatographic analysis.

#### QUANTIFICATION

The gas chromatograph used for analysis was a Packard model 7610 equipped with an electron-capture detector. The glass column, 6 ft by ¼ in., was packed with 2 percent OV-101 on 100/120 mesh Gas-Chrom Q and had a nitrogen carrier gas flow rate of 100 cc/min. Injection port, column, and detector temperatures were 215°, 190°, and 208°C, respectively. The method can detect 0.01 ppm mirex in a 1.0-g sample.

Mirex, which had been added to insects and to fat, brain, liver, and muscle of birds at levels of 0.01-1.0 ppm, was recovered at a rate of 90-100 percent. The identity of mirex was confirmed occasionally by determining a p-value.

### *Results and Discussion*

Mirex residues were found in 10 of the 28 species represented by the 49 pretreatment samples taken in Worth County. One year after treatment, residues in six of these same species were equal to or lower than those in pretreatment samples. In the other samples residues were relatively low 1 year after treatment; 62 percent had less than 0.05 ppm mirex and 92 percent had less than 0.5 ppm. Residues in the pretreatment samples probably resulted from treatment of fire ant mounds by landowners, since this area had not received any large-scale treatments. As noted, pretreatment samples from the Turner and Tift County test areas were cross-contaminated by isopropanol collection and were discarded. The pooled findings did not lend themselves to statistical analysis, and none was attempted. The majority of the 248 post-treatment samples, 71.77 percent, contained mirex residues.

As shown in Tables 4-11, maximum levels of mirex were reached 1 month after treatment, though in a few small vertebrates they were noted 3-6 months after treatment. Among the invertebrates, nymphal ground crickets had the highest residues (Table 4). Two specimens of *Pictonemobius ambitiosus* had residues of 13.20 ppm and 10.20 ppm 7 days after treatment and another cricket nymph in the subfamily Nemobinae had residues of 12.87 ppm 3 months after treatment. Residues were generally higher in crickets than in the other arthropods; wood cockroaches had the second-highest residues. Most arthropods analyzed are omnivorous feeders. Crickets and other arthropods were often found in the old mounds after the ants had died; they probably had fed on the dead ants or the remnants of the bait still in the mound.

The *Neonemobius* near *mormonius* (Table 4) and *Gryllus rubens* (Table 5) crickets have at least two generations of young each year in southwest Georgia. Thus the specimens of these two species taken 1 year after treatment almost certainly had not yet hatched at the time of treatment, and the Nemobinae cricket nymph (Table 4) taken 3 months after treatment probably hatched after the bait applications. It seems likely that the residues noted in these cases were acquired by crickets inhabiting the old mounds as previously described.

*Labidura riparia* has been found to transfer food by trophallaxis to the nymphs (*17*). Such transfer could

TABLE 4. *Mirex residues in crickets of subfamily Nemobinae according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Pictonemobius ambitiosus (adult ground crickets)** | | | | | | | | |
| Tift | May | 1.12 | D | 0.36 (1)<br>1.92 (1)<br>5.40 (1) | | 0.15 (3) | | |
| Tift | May | 1.68 | D | ND (1) | 5.73 (1) | | | |
| Turner | May- | 2.10 | D | | 3.40 (1) | 0.15 (10) | | |
| Turner | June | 4.20 | | | | 0.91 (2) | | |
| Worth | October | 1.12 | 1.76 (1) | | 2.06 (2) | | | |
| Worth | October | 4.20 | ND (4) | | | | | ND (1) |
| **Pictonemobius ambitiosus (nymphal ground crickets)** | | | | | | | | |
| Tift | May | 1.12 | | 13.20 (1) | | ND (1) | | |
| Tift | May | 1.68 | | 10.20 (1) | | | | |
| Turner | May- | 2.10 | | | 1.26 (6) | | | |
| Turner | June | 4.20 | | | 6.08 (5)<br>ND (1) | | | |
| Worth | October | 1.12 | ND (5) | | ND (1) | | ND (3) | |
| Worth | October | 4.20 | ND (4) | | | | 0.01 (3) | |
| **Neonemobius near mormonius (adult ground crickets)** | | | | | | | | |
| Tift | May | 1.12 | D | | | ND (1) | | |
| Tift | May | 1.68 | D | 2.08 (1)<br>3.11 (1) | 0.59 (2)<br>1.43 (1)<br>3.90 (2) | 2.26 (1) | | |
| Turner | May- | 2.10 | D | D | ND (6) | ND (4) | | |
| Turner | June | 4.20 | D | D | | | | |
| Worth | October | 1.12 | ND (5) | | 1.01 (1) | | ND (5) | 0.98 (1) |
| Worth | October | 4.20 | ND (1) | | | | 0.63 (2) | ND (1) |
| **Crickets of subfamily Nemboniae (nymphal ground crickets)** | | | | | | | | |
| Tift | May | 1.12 | D | | | 1.06 (1) | | |
| Tift | May | 1.68 | D | | ND (1) | | | |
| Turner | May- | 2.10 | D | D | ND (1)<br>0.84 (29)<br>0.86 (9)<br>1.81 (4) | ND (4)<br>12.87 (1) | | |
| Turner | June | 4.20 | D | D | 1.28 (14) | ND (30) | | |
| Worth | October | 1.12 | ND (7) | | 1.84 (7) | | ND (3) | ND (12) |
| Worth | October | 4.20 | ND (45) | | ND (5) | | | ND (3) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

account for the residues of mirex found in samples of earwigs (Table 8) 1 year after treatment. The presence of relatively high residues, 21.50 ppm, in shrews (Table 10) was not surprising, since these mammals are insectivores and would be expected to exhibit some biological concentration of mirex. Authors do not know whether the lower levels noted 3 months and 6 months after treatment are an indication of metabolism and excretion or of population turnover.

The residues found in terrestrial and semiterrestrial reptiles and amphibians (Table 10) probably resulted from biological concentration following consumption of animals that contained lower residues. The highest levels in these organisms were noted in cricket frogs (Table 10); slightly lower levels were found in narrow-mouth toads. Residues in all these animals 1 year after treatment were below 0.5 ppm except in one black snake which had 1.16 ppm mirex.

The semiaquatic and aquatic vertebrates (Table 11) generally contained low levels of residues. The highest levels were detected in mosquito fish (Table 11). The only other aquatic animal that contained more than 0.5 ppm mirex was a single specimen of leopard frog which had 1.08 ppm (Table 11) 3 months after treatment. Residues in all aquatic animals 1 year after treatment were 0.09 ppm or less.

Mirex residues appeared relatively quickly in all levels of the ecosystem studied. However, maximum levels appeared in the various organisms at different intervals after treatment, depending to a large extent on the niche occupied by the organism in the food chain. The levels of mirex detected in the organisms 1 year after treatment were comparable to those found by Baetcke et al. (5) and Collins et al. (7).

All specimens analyzed were taken alive or entered pitfall traps alive, and demonstrated no obvious effects

from mirex residues present. Authors observed no mass mortality of nontarget organisms in the field after treatments nor received reports of such mortality. No substantial differences were noted in the population size of any given species when it was tested before treatment and again 1 year after treatment.

No appreciable differences were noted in the residues in nontarget organisms as a result of applications of the various bait formulations. Indeed, amounts detected in the organisms from the area that received the latex-coated 0.1 percent mirex bait were comparable to those detected in organisms from the area that received the standard 0.3 percent mirex bait. This appears to substantiate the observations of Banks et al. (*13*) that less mirex is bound up in the corncob grits and thus more mirex is available to the ants in the latex-coated baits.

Even though residue levels were comparable, it seems logical to assume that the 75 percent reduction in toxicant load afforded by the 0.1 percent mirex bait must result in less environmental contamination. Since the 0.1 percent mirex bait provides excellent control of the ants (*13*), it should be an environmentally acceptable substitute for the standard mirex formulation.


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(*17*) *Shepard, M., V. Waddill, and W. Kloft. 1973.* Biology of the predaceous earwig *Labidura riparia* (Dermaptera: Labiduridae). Ann. Entomol. Soc. Amer. 66(4): 837-841.

TABLE 5. *Mirex residues in crickets of subfamily Gryllinae according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Gryllus rubens (adult southern field crickets)** | | | | | | | | |
| Tift | May | 1.12 | D | | 0.23 (4) | | | |
| Tift | May | 1.68 | D | | | 0.01 (15) | | |
| Turner | May- | 2.10 | D | | 0.27 (1) | 0.01 (26) | | |
| Turner | June | 4.20 | D | | | 0.03 (4) | | |
| Worth | October | 1.12 | 0.02 (12) | | | | ND (17) | ND (22) |
| Worth | October | 4.20 | ND (8) | | | | 0.05 (29) | ND (39) |
| **Gryllus fultoni (adult southern field crickets)** | | | | | | | | |
| Tift | May | 1.12 | | 1.04 (1) | | | | |
| Worth | October | 1.12 | ND (22) | | | | | ND (1) |
| Worth | October | 4.20 | ND (1) | | | | | ND (1) |
| **Gryllus firmus (adult sand crickets)** | | | | | | | | |
| Tift | May | 1.12 | | | | ND (3) | | |
| Tift | May | 1.68 | | | 0.06 (4) | 0.02 (36) | | |
| Turner | May- | 2.10 | D | | 0.18 (16) | | | |
| Turner | June | 4.20 | D | D | 0.41 (2) | | | |
| Worth | October | 1.12 | ND (15) | | 0.27 (7) | | 0.05 (2) | 0.04 (10) |
| Worth | October | 4.20 | ND (32) | | | | ND (1) | 0.03 (21) |
| **Miogryllus verticalis (stripe-headed crickets)** | | | | | | | | |
| Worth | October | 1.12 | | | | | | ND (2) (adults) ND (8) (nymphs) |
| Worth | October | 4.20 | | | | | | ND (6) (nymphs) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 6. *Mirex residues in mole crickets according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Scapteriscus acletus (adult and nymphal southern mole crickets)** | | | | | | | | |
| Tift | May | 1.68 | D | | | 0.18 (4) | | |
| Turner | May- | 2.10 | D | D | 0.53 (19) | 0.04 (6) | | |
| Turner | June | 4.20 | D | D | | 0.08 (4) | | |
| Worth | October | 1.12 | 0.10 (13) | | 0.91 (2) | | 0.23 (2) | |
| Worth | October | 4.20 | ND (32) | | ND (3) | | 0.14 (9) | 0.09 (8) |
| **Scapteriscus vicinus (adult and nymphal changas)** | | | | | | | | |
| Tift | May | 1.68 | D | | 0.05 (1) 1.15 (2) | 0.58 (1) | | |
| Turner | May- | 2.10 | D | D | | 0.14 (1) 0.34 (2) | | |
| Turner | June | 4.20 | | | | ND (3) | | |
| Worth | October | 4.20 | ND (1) | | | | 0.06 (9) | ND (2) |
| **Gryllotalpa hexadactyla (adult northern mole crickets)** | | | | | | | | |
| Worth | October | 1.12 | 0.10 (6) | | | | | 0.13 (3) |
| Worth | October | 4.20 | ND (1) | | | | | ND (1) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 7. *Mirex residues in cockroaches according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Parcoblatta spp. (adult and nymphal wood cockroaches)** | | | | | | | | |
| Tift | May | 1.12 | D | 3.98 (1) | 0.78 (8) | ND (1) | | |
| Tift | May | 1.68 | D | 1.50 (2) | 3.74 (7) | 0.12 (2) | | |
| | | | | | 6.18 (2) | | | |
| Turner | May-June | 4.20 | | D | | 1.41 (2) | | |
| Worth | October | 1.12 | ND (3) | | 4.39 (2) | | 0.19 (6) | ND (2) |
| Worth | October | 4.20 | ND (3) | | | | 0.22 (1) | ND (2) |
| | | | | | | | 0.60 (5) | |
| **Cariblatta lutea (adult small yellow cockroaches)** | | | | | | | | |
| Tift | May | 1.12 | D | | ND (1) | | | |
| Worth | October | 4.20 | | | | | ND (3) | |
| **Chorisoneura texensis (adult small yellow Texas cockroaches)** | | | | | | | | |
| Tift | May | 1.68 | | | ND (1) | | | |
| **Ichnoptera deropeltiformis (adult dark wood cockroaches)** | | | | | | | | |
| Worth | October | 4.20 | | | | | 0.18 (1) | |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 8. *Mirex residues in earwigs according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Labidura riparia (adult and nymphal riparian earwigs)** | | | | | | | | |
| Tift | May | 1.12 | | | | 0.19 (29) | | |
| Tift | May | 1.68 | | | | 0.11 (4) | | |
| Turner | May- | 2.10 | D | | | ND (1) | | |
| | | | | | | 0.23 (8) | | |
| Turner | June | 4.20 | D | | 0.63 (3) | 0.08 (11) | | |
| Worth | October | 1.12 | 0.02 (48) | | ND (1) | | | 0.03 (33) |
| Worth | October | 4.20 | ND (214) | | ND (4) | | 0.85 (4) | 0.04 (168) |
| **Euborellia annulipes (adult and nymphal ringlegged earwigs)** | | | | | | | | |
| Tift | May | 1.12 | D | | 0.43 (15) | 0.14 (7) | | |
| Tift | May | 1.68 | D | | 2.25 (1) | 0.06 (49) | | |
| Turner | May- | 2.10 | D | D | | ND (27) | | |
| Turner | June | 4.20 | D | D | | ND (1) | | |
| | | | | | | 0.37 (2) | | |
| | | | | | | 0.61 (4) | | |
| Worth | October | 1.12 | 0.06 (93) | | | | 0.13 (12) | ND (18) |
| Worth | October | 4.20 | ND (11) | | 0.51 (3) | | ND (3) | 0.04 (27) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 9. *Mirex residues in miscellaneous invertebrates according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Posttreatment | | | | |
| | | | Pretreatment | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Ceuthophilus spp. (nymphal camel crickets)** | | | | | | | | |
| Tift | May | 1.68 | D | 1.75 (1) | 3.60 (1) | | | |
| Turner | May- | 2.10 | D | D | 0.40 (1) | | | |
| Turner | June | 4.20 | D | D | 0.66 (1) | | | |
| | | | | | 2.88 (2) | | | |
| Worth | October | 1.12 | ND (17) | | | | 0.12 (21) | ND (3) |
| Worth | October | 4.20 | ND (3) | | | | 0.01 (7) | ND (2) |
| **Prosapia bicincta (adult two-lined spittle bugs)** | | | | | | | | |
| Tift | May | 1.12 | | | ND (22) | ND (7) | | |
| Turner | May-June | 4.20 | | | | 3.23 (1) | | |
| Worth | October | 1.12 | ND (8) | | ND (1) | | | |
| Worth | October | 4.20 | ND (25) | | 0.58 (1) | | | |
| **Armadillidium vulgare (adult and immature pillbugs)** | | | | | | | | |
| Tift | May | 1.12 | D | | 0.04 (16) | 0.01 (10) | | |
| Tift | May | 1.68 | D | | 0.03 (10) | 0.02 (5) | | |
| Turner | May-June | 2.10 | | D | ND (1) | ND (1) | | |
| Worth | October | 1.12 | ND (1) | | | | | |
| **Earthworms** | | | | | | | | |
| Tift | May | 1.12 | | 0.02 (10) | 0.49 (20) | 0.04 (25) | | |
| Tift | May | 1.68 | | | ND (26) | 0.03 (10) | | |
| Turner | May- | 2.10 | D | | 0.10 (20) | | | |
| Turner | June | 4.20 | | D | | 0.49 (10) | | |
| Worth | October | 1.12 | ND (50) | | ND (1) | | 0.02 (10) | ND (18) |
| Worth | October | 4.20 | ND (1) | | ND (1) | | 0.03 (10) | |
| **Latrodectus mactans (black widow spider)** | | | | | | | | |
| Worth | October | 1.12 | | | | | | 0.28 (3) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 10. *Mirex residues in terrestrial and semiterrestrial vertebrates according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Cryptotis parva (least shrews)** | | | | | | | | |
| Tift | May | 1.12 | | | 21.50 (1) | | | |
| Tift | May | 1.68 | D | | | 5.16 (1) | | |
| Worth | October | 1.12 | ND (1) | | | | | |
| Worth | October | 4.20 | ND (2) | | | | 1.15 (1) | |
| | | | | | | | 0.78 (1) | |
| **Cnemidophorus sexlineatus (6-lined racerunners)** | | | | | | | | |
| Turner | May- | 2.10 | D | D | | 0.93 (1) | | |
| Turner | June | 4.20 | | D | 0.63 (1) | 0.07 (1) | | |
| Worth | October | 1.12 | ND (1) | | | | | |
| Worth | October | 4.20 | ND (1) | | | | | 0.40 (1) |
| **Scincella laterale (brown skinks)** | | | | | | | | |
| Tift | May | 1.12 | D | | | 0.34 (1) | | |
| Worth | October | 1.12 | ND (2) | | | | 0.22 (4) | ND (1) |
| Worth | October | 4.20 | ND (3) | | | | 0.66 (1) | |
| **Eumeces laticeps (greater 5-lined skink)** | | | | | | | | |
| Worth | October | 1.12 | | | | | ND (1) | |
| **Coluber constrictor (black snake)** | | | | | | | | |
| Worth | October | 1.12 | | | | | | 1.16 (1) |
| **Natris sipedon fasciata (banded water snake)** | | | | | | | | |
| Turner | May-June | 4.20 | | D | 0.04 (1) | | | |
| **Bufo terrestris (southern toads)** | | | | | | | | |
| Turner | May-June | 2.10 | D | D | 0.94 (5) | | | |
| Turner | May-June | 4.20 | D | | 0.10 (1) | 0.39 (1) | | |
| Worth | October | 1.12 | ND (3) | | 0.24 (5) | | 0.02 (2) | |
| Worth | October | 4.20 | | | | | ND (1) | |
| **Gastrophryne carolinensis (narrow-mouth toads)** | | | | | | | | |
| Tift | May | 1.12 | D | | | 0.47 (2) | | |
| Tift | May | 1.68 | D | | | 3.46 (3) | | |
| Turner | May- | 2.10 | D | D | 2.02 (9) | 0.41 (14) | | |
| Turner | June | 4.20 | | | 0.33 (1) | 1.06 (2) | | |
| Worth | October | 1.12 | ND (16) | | | | | 0.17 (4) |
| Worth | October | 4.20 | 0.12 (5) | | | | | 0.04 (1) |
| **Pseudoacris ornata (ornate chorus frog)** | | | | | | | | |
| Worth | October | 1.12 | | | | | 0.10 (1) | |
| **Acris gryllus (cricket frogs)** | | | | | | | | |
| Worth | October | 1.12 | | | 9.27 (2) | | 0.14 (3) | |
| Worth | October | 4.20 | | | 3.01 (9) | | | |
| **Bufo quercicus (oak toads)** | | | | | | | | |
| Worth | October | 1.12 | | | | | | ND (5) |
| Worth | October | 4.70 | | | | | | 0.08 (2) |

NOTE: D = discarded cross-contaminated samples.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

TABLE 11. *Mirex residues in semiaquatic and aquatic vertebrates according to test site, Georgia—1971-72*

| County | Month of Application, 1971 | Mirex Applied, g/ha. | Residues, ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Pretreatment | Posttreatment | | | | |
| | | | | 7 Days | 1 Mo | 3 Mos | 6 Mos | 1 Yr |
| **Rana sphenocephala (Leopard frogs)** | | | | | | | | |
| Tift | May | 1.68 | | | | 0.08 (1) | | |
| Turner | May- | 2.10 | | D | | 1.08 (1) | | |
| Turner | June | 4.20 | | | 0.24 (1) | | | |
| Worth | October | 1.12 | | | | 0.56 (1) | | |
| Worth | October | 4.20 | ND (1) | | 0.34 (1) | | | |
| **Rana catesbeiana (bullfrogs)** | | | | | | | | |
| Tift | May | 1.12 | | | 0.05 (1) | | | |
| Tift | May | 1.68 | | | | 0.15 (4) | | |
| Turner | May-June | 2.10 | D | | 0.43 (1) | | | |
| Worth | October | 1.12 | ND (4) | | 0.08 (12) | | | 0.03 (6) |
| Worth | October | 4.20 | | | 0.25 (3) | | | 0.09 (1) |
| **Gambusia affinis (mosquito fish)** | | | | | | | | |
| Tift | May | 1.12 | D | | ND (10) | 0.11 (18) | | |
| Tift | May | 1.68 | D | | 0.06 (25) | ND (150) | | |
| Turner | May- | 2.10 | D | | 0.02 (20) | | | |
| | | | | | 0.08 (25) | | | |
| Turner | June | 4.20 | D | | 0.08 (20) | 0.24 (24) | | |
| Worth | October | 1.12 | ND (25) | | 0.25 (3) | | 2.93 (125) | ND (1) |
| Worth | October | 4.20 | 0.15 (15) | | 2.25 (10) | | 1.75 (105) | ND (6) |
| | | | | | | | | 0.03 (30) |
| **Lepomis macrochirus (bluegills)** | | | | | | | | |
| Tift | May | 1.12 | D | | ND (69) | | | |
| | | | | | 0.23 (10) | | | |
| Tift | May | 1.68 | D | | | ND (12) | | |
| Turner | May-June | 2.10 | D | | ND (5) | | | |
| Worth | October | 1.12 | | | | | ND (14) | 0.05 (4) |
| Worth | October | 4.20 | 0.03 (7) | | | | 0.02 (16) | ND (1) |
| | | | | | | | | 0.03 (2) |
| | | | | | | | | 0.03 (5) |
| **Fundulus lineolatus (lined topminnows)** | | | | | | | | |
| Tift | May | 1.12 | D | | 0.05 (9) | | | |
| Tift | May | 1.68 | | | | 0.04 (10) | | |
| Turner | May- | 2.10 | | | 0.21 (5) | | | |
| | | | | | 0.17 (10) | | | |
| Turner | June | 4.20 | D | | 0.03 (2) | | | |
| Worth | October | 4.20 | 0.03 (2) | | | | | |
| **Lepomis cyanellus (green sunfish)** | | | | | | | | |
| Tift | May | 1.12 | | | 0.05 (1) | | | |
| Worth | October | 4.20 | | | 0.05 (1) | | | |
| **Lepomis marginatus (dollar sunfish)** | | | | | | | | |
| Turner | May-June | 4.20 | | | 0.15 (6) | | | |
| **Notemigonus crysoleucas (golden shiners)** | | | | | | | | |
| Worth | October | 1.12 | ND (7) | | | | 0.09 (11) | 0.02 (21) |
| Worth | October | 4.20 | ND (1) | | | | ND (8) | |
| **Micropterus salmoides** | | | | | | | | |
| Worth | October | 4.20 | | | | | | ND (5) |

NOTE: D = discarded cross-contaminated sample.
ND = no residues detected at 0.01 ppm level.
Figures in parentheses represent number of specimens in pooled sample.

# GENERAL

## *Chlorinated Hydrocarbon Residues in Fish, Crabs, and Shellfish of the Lower Fraser River, Its Estuary, and Selected Locations in Georgia Strait, British Columbia—1972-73*

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ABSTRACT

*Between August 1972 and September 1973, fish, crabs, and shellfish were collected from the lower Fraser River, its estuary, and selected areas of Georgia Strait in British Columbia. Samples were analyzed for aldrin, dieldrin, α- and γ-chlordane, p,p'-DDT, p,p'-DDE, p,p'-DDD, heptachlor, heptachlor epoxide, lindane, and polychlorinated biphenyls (PCB's). Of these, p,p'-DDT, p,p'-DDE, p,p'-DDD, heptachlor epoxide, and one PCB, Aroclor 1254, were detected in samples of many fish, crabs, and shellfish from the lower Fraser River and its estuary. Generally, compounds found in decreasing order of magnitude in samples from the Fraser River and its estuary were: PCB's, p,p'-DDE, heptachlor epoxide, p,p'-DDT, and p,p'-DDD. Greatest concentrations of these compounds occurred in biota from the waters adjacent to the City of Vancouver. With one exception, animals from Georgia Strait and those away from the immediate influence of Fraser River water contained no detectable levels of chlorinated hydrocarbons.*

### *Introduction*

Numerous investigators have found chlorinated hydrocarbon insecticides and their metabolites as well as polychlorinated biphenyls (PCB's) in a variety of aquatic organisms including freshwater and marine fish (*1, 2*), birds (*3, 4*), plankton (*4, 5*), mammals (*4, 6*), and various invertebrates (*7, 8*). Some of these studies have shown that biological matter concentrates chlorinated hydrocarbon residues from the aquatic milieu and magnifies them through the various trophic levels (*4-6*).

The presence and persistence of chlorinated hydrocarbons in various river systems, including their watersheds and estuaries, of the United States (*1, 2, 7*), and to a lesser extent Europe (*9, 10*), have also been demonstrated. However, except for several studies of Ontario Rivers (*11, 12*), such data are generally lacking for many of the watersheds, rivers, and estuaries of Canada, particularly rivers which drain relatively uninhabited areas. Such a river system is the Fraser, which originates in the Rocky Mountains and flows for much of its length through forested or range land. However, this river passes through areas of intense agricultural and industrial use as well as human habitation immediately before terminating in Georgia Strait (Fig. 1). This estuary is adjacent to greater Vancouver, a metropolitan area of approximately one million inhabitants, and receives most of that city's domestic and industrial effluents.

Thus, by studying this river system, one may determine chlorinated hydrocarbon residue levels in water, sediment, and biota in areas adjacent to low habitation, intensive agricultural production, and an urban population. Such data are essential for evaluating the significance of chlorinated hydrocarbons to the aquatic flora and fauna and are relevant in determining the suitability of this water for various uses.

### *Methods and Materials*

Fish were taken from the Fraser River with gill nets and seines and from Georgia Strait with bottom trawls. Most river fish were captured in gill nets set during the day near the river margin at each station (Fig. 1), although some were taken in seine hauls made near the same location. Within a few hours of capture, all fish were frozen.

After a specimen selected for analysis was thawed, measured, and weighed, its dorsolateral surface was scraped clean to remove any debris or slime. Then an area of epaxial white muscle tissue was exposed with a new scalpel which was cleaned with acetone. A block

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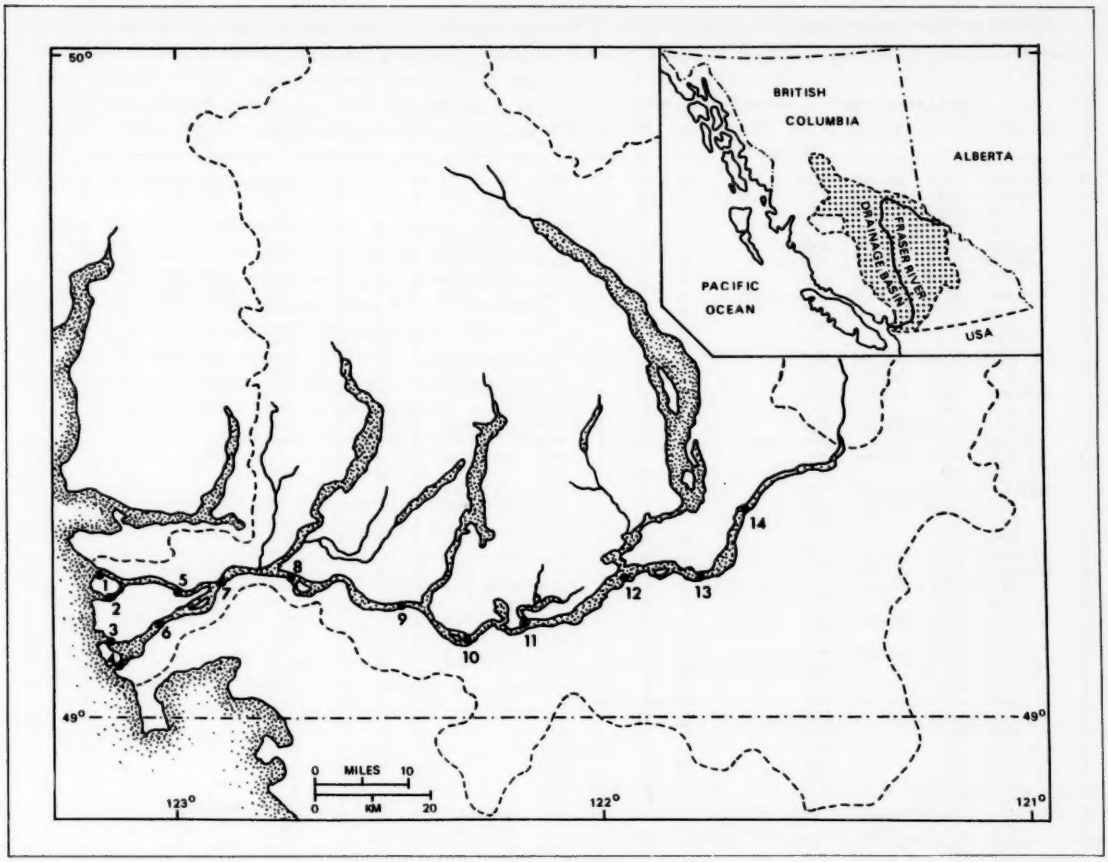


**FIGURE 1.** *Fraser River with sampling stations*

of approximately 25 g tissue was removed, placed in an externally labeled glass jar, and refrozen. Other animals, including shellfish and crabs, were obtained by scuba divers. Tissue samples were placed into glass jars and frozen. In some cases, entire animals were frozen for future analysis (Table 1). All glass containers were cleaned with redistilled hexane and acetone, then heated to 135°C for 12 hours prior to use.

Tissues were extracted with 50 ml of a 1:1 v/v hexane: acetone mixture for every 25 g sample tissue in a Lourdes homogenizer for 30 minutes. After 15 minutes, 25 g anhydrous $Na_2SO_4$ was added. Each extract was then filtered through glass wool into a 250-ml separatory funnel and washed twice with 50 ml of an aqueous solution of 2 percent $Na_2SO_4$.

Aliquots of each extract equivalent to 1 g tissue were then cleaned by a combination of sweep codistillation and column chromatography as described in detail for human adipose tissue extracts by Oloffs et al. (*13*). Finally, PCB's were separated from the other organochlorines according to the method of Armour and Burke (*14*).

The clean extracts were picked up with 2 ml hexane for every 1 g tissue extracted. Gas-liquid chromatographic (GLC) analyses were performed with a Tracor MT 220 and a Tracor 550 equipped with two and one $^{63}Ni$ electron-capture detectors, respectively. A 183-cm-by-0.64-cm column packed with 2 percent OV-1 and 6 percent OV-210 in 80/100 mesh chromosorb W HP was used. Nitrogen, the carrier gas, had a flow rate of 80 ml/min. The temperatures of the injector, column oven, and detector were 220°, 190°, and 300°C, respectively.

Standard curves were prepared daily before and after sample analyses with reference-grade chemicals in hexane. Residues were quantified to the following concentrations: heptachlor epoxide, 2 ppb; dieldrin, DDD, and DDE, 4 ppb; and DDT, 10 ppb. Aroclor 1254, the only PCB found in these samples, was quantified to 20 ppb standard Aroclor 1254 on the basis of four selected peaks as described and critically discussed by Iwata et al. (*15*).

If an injection of 8 $\mu$l of the 2 ml hexane : 1 g tissue extract gave a response for one of the compounds which

TABLE 1. *Chlorinated hydrocarbon concentrations in muscle tissue of fish, Fraser River, British Columbia—1972-73*

| Station No. | Species [1] | Fork Length, mm | | Heptachlor Epoxide | | | | | DDE | | | | | PCB's [5] | | | | No. Samples |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | |
| 14 | SQUAW | 337.5 | 262-440 | ND | | 0 | 0 | 17 | 56.2 | T -164.3 | 16 | 1 | 0 | 32.7 | ND- 234.7 | 5 | 5 | 7 | 17 |
| 14 | LSS [6] | 389.1 | 346-453 | 4.1 | ND-26.5 | 5 | 0 | 11 | 10.7 | ND- 55.3 | 8 | 1 | 7 | 138.0 | ND- 589.7 | 9 | 0 | 7 | 16 |
| 14 | RT | 279.0 | 256-302 | ND | | 0 | 0 | 2 | 5.9 | ND- 11.7 | 1 | 0 | 1 | 37.2 | T - 72.4 | 1 | 1 | 0 | 2 |
| 14 | CTT | 308 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | 1 |
| 14 | MW | 275.3 | 245-297 | ND | | 0 | 0 | 4 | 56.3 | 7.0-100.3 | 4 | 0 | 0 | ND | | 0 | 0 | 4 | 4 |
| 14 | CHUB | 255.5 | 254-257 | ND | | 0 | 0 | 2 | 106.0 | 57.5-154.4 | 2 | 0 | 0 | ND | | 0 | 0 | 2 | 2 |
| 14 | ST | 434.0 | 363-475 | ND | | 0 | 0 | 4 | 37.6 | 31.9- 40.0 | 4 | 0 | 0 | 41.7 | ND- 164.7 | 1 | 1 | 2 | 4 |
| 13 | SQUAW | 301.0 | 264-359 | 1.7 | ND-5.0 | 1 | 0 | 2 | 9.9 | T - 17.6 | 2 | 1 | 0 | 204.2 | ND- 526.7 | 2 | 0 | 1 | 3 |
| 13 | LSS | 335 | | ND | | 0 | 0 | 1 | 9.6 | | 1 | 0 | 0 | 349.8 | | 1 | 0 | 0 | 1 |
| 13 | BBH | 246 | | ND | | 0 | 0 | 1 | 3.5 | | 1 | 0 | 0 | 235.3 | | 1 | 0 | 0 | 1 |
| 13 | CARP | 492 | | ND | | 0 | 0 | 1 | 53.5 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 13 | RT [7] | 316.5 | 245-394 | ND | | 0 | 0 | 8 | 20.3 | ND- 48.8 | 6 | 0 | 2 | 58.9 | ND- 229.2 | 3 | 4 | 1 | 8 |
| 13 | CHUB | 260.3 | 242-277 | ND | | 0 | 0 | 3 | 44.4 | 26.7- 62.8 | 3 | 0 | 0 | ND | | 0 | 0 | 3 | 3 |
| 12 | SQUAW | 286.3 | 261-355 | ND | | 0 | 0 | 6 | 48.2 | ND-144.7 | 5 | 0 | 1 | 0.3 | ND-T | 0 | 1 | 5 | 6 |
| 12 | LSS | 320 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 1 |
| 12 | MW | 258.5 | 252-265 | ND | | 0 | 0 | 2 | 28.9 | 27.5- 30.3 | 2 | 0 | 0 | ND | | 0 | 0 | 2 | 2 |
| 12 | CHUB | 258 | | ND | | 0 | 0 | 1 | 49.6 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 12 | ST | 400.7 | 356-464 | ND | | 0 | 0 | 3 | 18.1 | 15.0- 22.9 | 3 | 0 | 0 | 1.3 | ND-T | 0 | 2 | 1 | 3 |
| 11 | LSS | 330 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 1 |
| 11 | SQUAW | 325.0 | 286-364 | ND | | 0 | 0 | 2 | 37.2 | 4.9- 59.4 | 2 | 0 | 0 | ND | | 0 | 0 | 2 | 2 |
| 11 | RT | 356.5 | 276-442 | ND | | 0 | 0 | 4 | 32.1 | 6.9- 59.5 | 4 | 0 | 0 | 0.5 | ND-T | 0 | 1 | 3 | 4 |
| 11 | CTT | 311 | | ND | | 0 | 0 | 1 | 14.4 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 11 | MW | 253 | | ND | | 0 | 0 | 1 | 20.3 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 11 | CHUB | 257.5 | 249-266 | ND | | 0 | 0 | 2 | 32.1 | 22.1- 42.1 | 2 | 0 | 0 | ND | | 0 | 0 | 2 | 2 |
| 10 | SQUAW | 320.5 | 313-328 | ND | | 0 | 0 | 2 | 36.4 | 11.5- 61.3 | 2 | 0 | 0 | 83.8 | ND- 167.5 | 1 | 0 | 1 | 2 |
| 10 | RT [8] | 293.3 | 253-418 | 2.3 | ND-10.7 | 3 | 0 | 9 | 7.3 | ND- 29.4 | 8 | 2 | 2 | 61.7 | ND- 106.2 | 9 | 0 | 3 | 12 |
| 10 | ST | 438 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 1 |
| 10 | LSS | 317.5 | 275-360 | 4.6 | ND- 9.1 | 1 | 0 | 1 | 7.5 | ND- 14.9 | 1 | 0 | 1 | 147 | ND- 294.0 | 1 | 0 | 1 | 2 |
| 10 | DV | 337 | | ND | | 0 | 0 | 1 | 19.5 | | 0 | 0 | 1 | 164.3 | | 1 | 0 | 0 | 1 |
| 9 | RT | 283.3 | 275-288 | ND | | 0 | 0 | 3 | 8.9 | ND- 14.5 | 2 | 0 | 1 | ND | | 0 | 0 | 3 | 3 |
| 9 | LSS | 368 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 3694.9 | | 1 | 0 | 0 | 1 |
| 9 | CHUB | 263 | | ND | | 0 | 0 | 1 | 37.3 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 8 | MW | 192 | | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | ND | | 0 | 0 | 1 | 1 |
| 8 | ST | 355 | | ND | | 0 | 0 | 1 | 21.8 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 8 | LSS | 364 | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 623.4 | | 1 | 0 | 0 | 1 |
| 8 | SQUAW | 288 | | ND | | 0 | 0 | 1 | 329.3 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 8 | CHUB | 233 | | ND | | 0 | 0 | 1 | 34.7 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 7 | ST | 455 | | ND | | 0 | 0 | 1 | 10.6 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 7 | CHUB | 247 | | ND | | 0 | 0 | 1 | 33.4 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 7 | RT [9] | 344.4 | 273-400 | 12.4 | ND-44.9 | 3 | 0 | 2 | 34.9 | ND- 50.1 | 4 | 0 | 1 | 143.2 | 58.2- 192.8 | 5 | 0 | 0 | 5 |
| 7 | CTT [10] | 423.7 | 319-565 | 4.7 | ND-13.7 | 2 | 0 | 2 | 19.8 | ND- 43.5 | 3 | 0 | 1 | 128.2 | 77.1- 208.5 | 4 | 0 | 0 | 4 |
| 6 | LSS | 308.7 | 302-314 | ND | | 0 | 0 | 3 | ND | | 0 | 0 | 3 | 171.2 | ND- 259.4 | 2 | 0 | 1 | 3 |
| 6 | SQUAW [7] | 279.8 | 183-340 | ND | | 0 | 0 | 5 | 85.0 | 8.8-151.7 | 5 | 0 | 0 | 748.4 | 204.1-1894.4 | 5 | 0 | 0 | 5 |
| 6 | ST | 413.0 | 390-436 | ND | | 0 | 0 | 2 | 11.8 | ND- 23.5 | 1 | 0 | 1 | 143.4 | ND- 286.7 | 1 | 0 | 1 | 2 |
| 5 | LSS | 417.8 | 374-453 | ND | | 0 | 0 | 4 | 7.2 | T - 16.9 | 3 | 1 | 0 | 90.6 | T - 198.7 | 2 | 1 | 1 | 4 |
| 5 | DV | 422 | | ND | | 0 | 0 | 1 | 17.5 | | 1 | 0 | 0 | ND | | 0 | 0 | 1 | 1 |
| 5 | ST | 438.5 | 419-458 | 4.2 | ND- 8.3 | 1 | 0 | 1 | 22.9 | 3.4- 42.3 | 2 | 0 | 0 | 167.4 | 136.9- 197.8 | 2 | 0 | 0 | 2 |
| 5 | RT [11] | 282.5 | 282-283 | 3.3 | ND- 6.5 | 1 | 0 | 1 | 7.4 | 6.8- 8.0 | 2 | 0 | 0 | 128.9 | 64.8- 192.9 | 2 | 0 | 0 | 2 |
| 5 | SQUAW [12] | 351.5 | 344-359 | 4.3 | ND- 8.6 | 1 | 0 | 1 | 238.3 | 39.5-437.1 | 2 | 0 | 0 | 1039.8 | 426.7-1652.9 | 2 | 0 | 0 | 2 |
| 5 | CARP [11] | 557 | | ND | | 0 | 0 | 1 | 1739.6 | | 1 | 0 | 0 | 933.9 | | 1 | 0 | 0 | 1 |
| 4 | RT | 283 | | ND | | 0 | 0 | 1 | 20.0 | | 1 | 0 | 0 | 138.8 | | 1 | 0 | 0 | 1 |
| 4 | SQUAW | 217.8 | 153-367 | ND | | 0 | 0 | 4 | 36.4 | 3.8- 99.9 | 4 | 0 | 0 | 121.8 | ND- 483.2 | 1 | 2 | 1 | 4 |
| 3 | SOCK-EYE | 595.8 | 561-633 | ND | | 0 | 0 | 5 | ND | | 0 | 0 | 5 | ND | | 0 | 0 | 5 | 5 |
| 3 | CTT [13] | 362.5 | 344-381 | 4.5 | ND- 9.0 | 1 | 0 | 1 | 25.3 | 21.1- 29.4 | 2 | 0 | 0 | 118.6 | 101.7- 135.4 | 2 | 0 | 0 | 2 |
| 3 | CHUB | 225.3 | 211-253 | ND | | 0 | 0 | 3 | 43.4 | T - 69.9 | 2 | 1 | 0 | 90.8 | ND- 272.4 | 1 | 0 | 2 | 3 |
| 3 | CHI-NOOK | 394.5 | 389-400 | 2.2 | ND- 4.3 | 1 | 0 | 1 | 12.3 | 9.0- 15.5 | 2 | 0 | 0 | 86.8 | 83.5- 90.1 | 2 | 0 | 0 | 2 |
| 3 | SQUAW | 359.5 | 325-394 | 47.0 | 7.4-86.6 | 2 | 0 | 0 | 73.3 | 51.4- 95.2 | 2 | 0 | 0 | 755.4 | 607.6- 903.2 | 2 | 0 | 0 | 2 |
| 3 | LSS | 331.7 | 302-370 | ND | | 0 | 0 | 3 | 12.2 | ND- 36.5 | 1 | 0 | 2 | 153.9 | ND- 250.6 | 2 | 0 | 1 | 3 |
| 3 | ST [14] | 510.9 | 391-635 | 3.9 | ND- 7.1 | 3 | 0 | 6 | 14.9 | ND- 47.4 | 7 | 0 | 2 | 165.4 | ND- 317.7 | 7 | 0 | 2 | 9 |
| 2 | RT | 303.0 | 267-345 | 4.2 | ND-12.6 | 1 | 0 | 2 | 34.5 | T - 54.9 | 2 | 1 | 0 | 116.5 | T - 314.1 | 2 | 1 | 0 | 3 |
| 1 | CHUB | 237 | | ND | | 0 | 0 | 1 | 85.9 | | 1 | 0 | 0 | 527.3 | | 1 | 0 | 0 | 1 |

NOTE: ND = not detectable; T = trace.

[1] SQUAW = northern squawfish; LSS = large scale sucker; RT = rainbow trout; CTT = cutthroat trout; MW = mountain whitefish; CHUB = peamouth chub; ST = sturgeon; BBH = bullhead; DV = dolly varden.
[2] No. samples with concentrations >4 ppb (>20 ppb for Aroclor 1254).
[3] No. samples with a trace of residue.
[4] No. samples with no detectable residue.
[5] Similar to Aroclor 1254.
[6] One sample had a trace of DDT, four had a trace of DDD, and one had a trace of dieldrin.
[7] One sample had a trace of DDT.
[8] Three samples had a trace of DDT; five had a trace of DDD.
[9] Two samples had a trace of DDT, two had a trace of DDD, and one had traces of DDT and DDD.
[10] Three samples had a trace of DDT, three had a trace of DDD, and two had a trace of dieldrin.
[11] One sample had a trace of DDD.
[12] Two samples had a trace of DDT; one sample had a trace of DDD.
[13] One sample had traces of DDT and DDD.
[14] Three samples had a trace of DDT, three had a trace of DDD, and one had 9.7 ppb dieldrin.

was below the lowest amount of standard injected, approximately 5 percent chart deflection, it was designated a trace amount. If no response was observed, it was considered to be not detectable. For quantification of compounds with higher concentrations, hexane extracts were appropriately diluted to yield responses within the range of the injected standards.

Samples containing sufficiently high concentrations of DDE and Aroclor 1254 were checked by mass spectrometry. These spectra resembled those of the corresponding reference-grade compounds. The instrument was a Varian gas chromatograph series 1400 with an attached Hitachi Perkin-Elmer RMV-6E spectrometer. The column and packing remained the same for this study. A 183-cm-by-0.64-cm column packed with 2 percent OV-1 and 6 percent OV-210 was employed for confirmation.

Recoveries and the efficiency of separating Aroclor 1254 from the other compounds were checked periodically with tissue samples spiked with standards at concentrations near the lower limits of quantification. Average percentages of recovery were Aroclor 1254, 85.2; DDD, 89.2; dieldrin, 91.3; DDT, 91.4; DDE, 92.8; heptachlor epoxide, 93.9; aldrin, 94.3; lindane, 97.5; and heptachlor, 99.0. Recovery studies were occasionally done so that the person analyzing the samples did not know they were spiked.

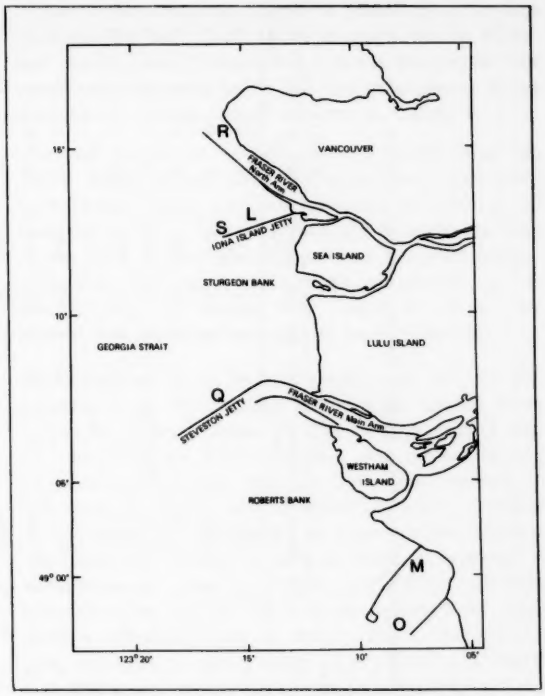


FIGURE 2. *Georgia Strait with sampling stations*

## *Results and Discussion*

Eichelberger and Lichtenberg (*16*) have shown that of 28 common pesticides including 12 organochlorines, 9 organophosphates, and 7 carbamates placed in raw river water for up to 8 weeks, all were degraded except chlorinated hydrocarbons BHC, heptachlor epoxide, dieldrin, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, and endrin, as well as the organophosphate monocrotophos. In addition to their greater resistance to degradation, these compounds also tend to accumulate in both plant and animal biota (*5*).

Data in Tables 1 and 2 indicate this as well. Although chlorinated hydrocarbons were not detected in waters or sediments of the lower Fraser River, its estuary, or Georgia Strait (*17-19*), dieldrin, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, heptachlor epoxide, and PCB's were found in many fish and benthic animal samples of the Fraser River and its estuary (Tables 1, 2). However, except for a very low mean level of *p,p'*-DDE in three of seven *Cancer magister* samples from station C (mean of 2.1 ppb), no chlorinated hydrocarbons were found in fish and crab samples from Georgia Strait and in an area away from the immediate influence of Fraser River water (Fig. 2, stations A, B, and C). Table 3 lists the fish and crabs analyzed. Chlordane, lindane, endrin, and aldrin were not detected in any of these samples.

Analysis of the data in Table 1 indicates that several chlorinated hydrocarbons were present to a greater extent than others in fish. Compounds in Fraser River estuary fish were found in the following order of decreasing concentrations: PCB's, *p,p* -DDE, heptachlor epoxide, *p,p'*-DDD, and *p,p'*-DDT (stations 1-7, Fig. 1, Table 1). Analysis of the relative concentrations of chlorinated hydrocarbons in other fauna of this estuary indicates a similar pattern (Fig. 3, Table 2). The order of decreasing concentrations of compounds in fish from the upper reaches (stations 13, 14, Fig. 1, Table 1) was PCB's, *p,p'*-DDE, heptachlor epoxide, *p,p'*-DDD, *p,p'*-DDT, and dieldrin. A similar pattern was noted for fish from the middle reaches (stations 8-12, Fig. 1, Table 1).

Clearly, PCB's and *p,p'*-DDE are the chlorinated hydrocarbons of major importance in the biota sampled within this aquatic system. Further analysis of the data in Table 1 indicates that the average PCB and *p,p'*-DDT residues in fish species from the estuary (stations 1-7) were significantly greater than those from the upper portion (stations 13, 14) of the Fraser River. These patterns of concentrations may reflect the uses of land adjacent to the river at each station. Most of the upper and middle reaches are adjacent to agricultural regions whereas the estuary is next to the urban and industrial region of greater Vancouver as well as agricultural land. Hence the relatively greater concentrations of chlori-

TABLE 2. *Chlorinated hydrocarbon concentrations in various faunal species, Fraser River estuary, British Columbia—1972-73*

| Station No. | Species [1] | Shell size, mm | | Heptachlor Epoxide | | | | | *p,p'* - DDE | | | | | PCB's [5] | | | | PCB's [6] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | Mean, ppb | Range, ppb | N [2] | N [3] | N [4] | Mean, ppb | N [2] | N [3] | N [4] | No. Samples |
| M | CC | 8 [7] | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 11.9 | 1 | 0 | 0 | 1 |
| M | CG | 11 [7] | | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | 2724.1 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |
| R | CM | 10.8 [8] | | ND | | 0 | 0 | 1 | 82.0 | | 1 | 0 | 0 | 105.3 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |
| Q | CM | 13.1 [8,9] | 9.5-16.1 | 7.7 | ND-22.0 | 2 | 0 | 3 | 95.6 | 23.0-295.8 | 5 | 0 | 0 | 781.8 | 234.2-2100.3 | 5 | 0 | 0 | ND | 0 | 0 | 5 | 5 |
| L | CC | all sizes [7,10] | | 23.0 | | 1 | 0 | 0 | 32.0 | | 1 | 0 | 0 | 295.0 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |
| L | ME | 4 [10,11] | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | ND | 0 | 0 | 1 | 1 |
| L | CS | 3 [7,10,12] | | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | 214.0 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |
| O | CCO | 9.5 [11,13] | | ND | | 0 | 0 | 1 | ND | | 0 | 0 | 1 | 193.0 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |
| O | CM | 13.5 [8] | 11.9-15.5 | 3.3 | ND-18.9 | 2 | 0 | 5 | 36.8 | ND-141.1 | 5 | 1 | 1 | 559.3 | 170.1-1375.4 | 7 | 0 | 0 | ND | 0 | 0 | 7 | 7 |
| S | CM | 15.4 [8,9] | 14.8-16.1 | 3.7 | ND-11.4 | 2 | 0 | 3 | 101.4 | 23.1-176.9 | 5 | 0 | 0 | 839.7 | 154.3-1607.1 | 5 | 0 | 0 | ND | 0 | 0 | 5 | 5 |
| S | CG | 13 [7,14] | | ND | | 0 | 0 | 1 | T | | 0 | 1 | 0 | 322.3 | | 1 | 0 | 0 | ND | 0 | 0 | 1 | 1 |

NOTE: ND = not detectable; T = trace.

[1] CC = *Callianassa californiensis;* CG = *Crassostrea gigas;* CM = *Cancer magister;* ME = *Mytilus edulis;* CS = *Citharichthyes stigmaeus;* and CCO = *Cardium corbis.*
[2] No. samples with concentrations > 4 ppb.
[3] No. samples with trace of residue.
[4] No. samples with no detectable residue.
[5] Similar to Aroclor 1254.
[6] Similar to Aroclor 1242.
[7] Entire animal assayed.
[8] Hepatopancreas assayed.
[9] One sample had a trace of dieldrin.
[10] More than one individual in this sample.
[11] Soft tissue assayed.
[12] Body length.
[13] Two samples had traces of *p,p'*-DDD.
[14] One sample had a trace of *p,p'*-DDT.

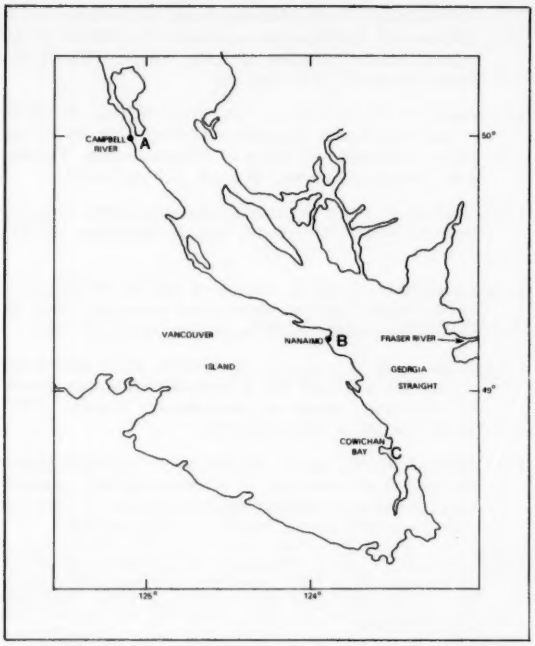


FIGURE 3. *Fraser River estuary with sampling stations*

nated hydrocarbons in estuarine fish may reflect increased residue levels in estuarine water compared to water from the upper reaches of the Fraser River.

Chlorinated hydrocarbons are believed to enter water bodies, including rivers, via rainfall, surface runoff, aerial sprays, ground water, direct application for insect control, and domestic and industrial effluents. However, the most probable pathways by which PCB's enter the Fraser River and its estuary are by surface runoff and domestic and industrial effluents from the Vancouver region. The storm and sewage lines of the city of Vancouver combine and terminate in an outfall near station L (Fig. 3). PCB residues in fauna were highest in animals from this estuary; their concentration appears to be proportional to the distance of the sampled benthic animals from the outfall. Exemplary are levels of *C. magister* at stations O, Q, S, and R, and *Callinanassa*

TABLE 3. *Fish and crabs sampled from Georgia Strait and areas away from the immediate influence of Fraser River water, British Columbia—1972-73*

| Species | Station | Fork Length or Shell Width, cm | No. Individuals Analyzed |
|---|---|---|---|
| Red snapper | A | 36 | 1 |
| Sole | A | 24 | 1 |
| Ratfish | A | 37 | 1 |
| Tomcod | A | 36 | 1 |
| Skate | A | 62 | 1 |
| Rockfish | A | 37.5 | 2 |
| Coho salmon | B | 46 | 3 |
| Ratfish | C | 30.6 | 5 |
| Rockfish | C | 23.5 | 2 |
| *Cancer magister* | C | 11.2 | 7 |

*californiensis* at stations L and M (Table 2). It is thus possible that one major route through which PCB's, and possibly other chlorinated hydrocarbons, enter this water and are taken up by fish and other biota, is the Iona Island sewage outfall adjacent to station L.

The two species of salmon adults sampled from the Fraser River estuary contained either low chlorinated hydrocarbon levels (chinook salmon) or none at all (sockeye salmon, Table 1). Because chinook are only in the river as juvenile migrants and are only temporarily near the estuary and sockeye are present only as juvenile migrants before they return as adults, the general low levels in these species seem reasonable.

Henderson et al. (*1*) have shown that of 147 fish removed from 50 sampling locations on various rivers across the United States, all contained *p,p'*-DDT and its metabolite *p,p'*-DDE. Dieldrin was present in 137 of these 147 samples whereas BHC was reported in fish from 15 stations only. Heptachlor epoxide residues were present in six samples at three stations whereas chlordane was present in samples from six stations. A calculation of mean *p,p'*-DDE, *p,p'*-DDT, and PCB concentrations in fish from levels reported by these authors revealed values of 692.9, 289.6, and 1,254.8 ppb, respectively. Mean values of *p,p'*-DDE, *p,p'*-DDT, and PCB's reported in this investigation of Fraser River fish were very much lower at 40.5, 0.3, and 140.8 ppb, respectively.

Henderson et al. (*1*) have further shown that *p,p'*-DDT levels in fish vary widely, depending upon the river in question. However, reported values for *p,p'*-DDT and *p,p'*-DDE in the 50 United States rivers sampled were all greater than values in fish from the Fraser River.

Studies of Long Island estuaries (*7*) and several California estuaries (*2*) revealed that shellfish and fish sampled from these waters also tended to concentrate chlorinated hydrocarbons in their tissues. In both areas levels of *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and dieldrin were determined in animal tissue. In addition, many fish and shellfish removed from the California marine estuaries contained endrin (*2*).

Authors' analyses indicated the presence of only *p,p'*-DDE, heptachlor epoxide, and PCB's in fish and other benthic animals from the Fraser River estuary although several samples contained trace residues of *p,p'*-DDT, *p,p'*-DDD, and dieldrin. However, concentrations of *p,p'*-DDE were approximately equivalent to those reported by Modin (*2*) for *C. magister* removed from the California coast in the vicinity of San Francisco.

Miles and Harris (*12*), working with agricultural, urban-agricultural, and resort rivers in Ontario, found a more extensive pattern of chlorinated hydrocarbon insecticides than authors have noted for the lower Fraser River system. In addition to *p,p'*-DDE, heptachlor

epoxide, *p,p'*-DDT, *o,p'*-DDE, and *p,p'*-TDE, they detected *o,p'*-DDT, *o,p'*-TDE, *p,p'*-TDE, α-chlordane, and endrin in sampled fish whereas the authors of the present study did not. The one river in which they detected PCB's in fish was the Thames River, which is urban-agricultural as is the lower part of the Fraser River. PCB contamination of water, and hence fish and other aquatic fauna, appears to be more closely associated with rivers adjacent to urban areas than with agricultural or forested land.


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# *Mirex Residues in Wildlife and Soils, Hawaiian Pineapple-Growing Areas—1972-74* [1,2]

Arthur Bevenue, James N. Ogata, Lester S. Tengan, and John W. Hylin


## ABSTRACT

*A monitoring program was conducted in the pineapple-growing areas of Hawaii from 1972 to 1974 to survey mirex residues in sediments, soils, and aquatic and terrestrial wildlife. Residues in pineapple field soils ranged from 3 to 18 ppb 9 months after mirex had been applied. No residues were found in the sediments. Only 8 fish of 110 aquatic animals sampled contained mirex; these levels were low and ranged from 3 to 7 ppb. Mirex residues in birds ranged from undetectable to 10 ppm; residues in rodents were quite variable, but in terms of the geometric mean, the amounts in the Polynesian rat decreased with time from 1,270 to 56 ppb. Similarly, values for the roof rat ranged from 666 to 17 ppb. The geometric mean for residues in mongooses decreased from 2,200 ppb immediately after application to 238 ppb 39 weeks later. Aerial application of mirex to the pineapple fields did not contaminate the marine environment of Hawaii and no evidence of mirex residue buildup in the aquatic food chain was apparent. Mirex accumulation in terrestrial biota was temporary; there was no definitive indication of permanent accumulation in the wildlife of the areas studied.*


## *Introduction*

Successful pineapple production requires the control of several insect-transmitted diseases, the most serious of which is mealybug wilt caused by the pineapple mealybug (*Dysmicoccus brevipes*). Direct control of this organism is not feasible, but because it is transported and protected by the bigheaded ant (*Pheidole megacephala*), the disease can be controlled by reducing the ant population in pineapple fields. Mirex has been successfully used for ant control in pineapple production in Hawaii since 1970. It was used on about 30,000 acres in 1972 when about 76,000 lb bait containing 220 lb mirex (0.29 percent active ingredient) was applied. The use of mirex in Hawaii was temporarily suspended in 1972 when the U.S. Environmental Protection Agency (EPA) permitted an exception to their Notice of Cancellation of registrations of pesticides containing mirex (March 18, 1971, and amended by two Determination and Orders on May 3, 1972, and June 30, 1972), provided that aerial application of mirex in the Hawaiian pineapple fields would be subjected to EPA approval. Monitoring procedures used for the 1972-74 pineapple-growing seasons and the analytical results of mirex residues in environmental specimens obtained from pineapple-growing areas are described in this report.

## *Sampling*

State areas pertinent to mirex monitoring are indicated in Figures 1-3. The 1972-73 samples included aquatic specimens, sediments, and soils; sampling was confined to two coastal areas on the island of Maui and one each on the islands of Molokai and Oahu. Samples were taken quarterly for 1 year.

The 1973-74 samples were primarily terrestrial vertebrates with some additional aquatic and soil samples. The second-year sampling program for soil and terrestrial biota was confined to the Maliko watershed area on the island of Maui, an area which contained 4,962 acres under pineapple production. Aquatic specimens were collected at both the Maliko and Honokohau areas. Soil and sediment samples were selected from sites where mirex would most likely be transported by streams from the fields to coastal areas. Sediment samples were taken near the shoreline areas at an approximate depth of 1 cm and placed in 1-quart cans which had been baked at 200°C. Topsoil samples were removed to a depth of about 1 cm from 9-ft$^2$ areas and were also stored in heat-treated cans. At least two samples were taken during each round of monitoring from two pineapple fields in an area where surface water runoff converged after exiting each field. Most

[1] Presented in part at the Third International Congress of Pesticide Chemistry, Helsinki, Finland, July 3-9, 1974. Journal Series No. 1858, Hawaii Agricultural Experiment Station.

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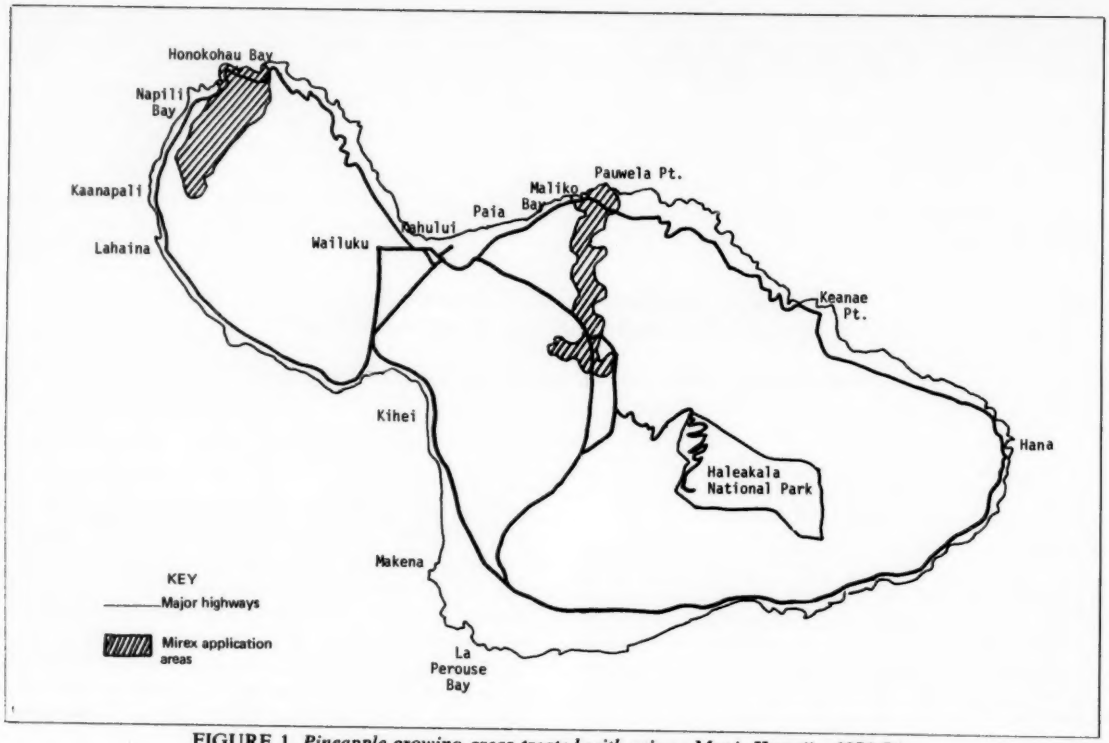


FIGURE 1. *Pineapple-growing areas treated with mirex, Maui, Hawaii—1972-74*

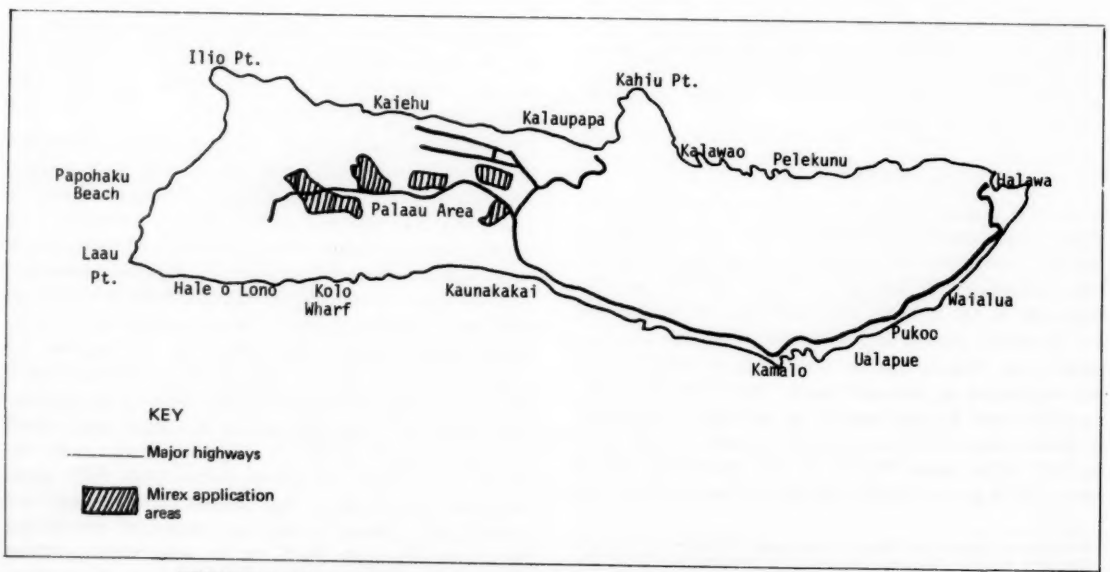


FIGURE 2. *Pineapple-growing areas treated with mirex, Molokai, Hawaii—1972-73*

of the fish, shrimp, and crabs were caught by either throw or scoop nets. Occasionally, spearfishing was substituted for netting. Algae and oysters were gathered by hand; birds were shot; and rodents and mongooses were obtained with snap and live traps, respectively. All animals were taken within the confines of a mirex-treated field.

Specimens were obtained 1 week before and 1-2 weeks after mirex application. Additional samples were taken at approximately 1-month intervals for a period of 9 months. All specimens were labelled and packaged separately, packed in ice in chilled insulated containers, and transported to the analytical laboratory within 24 hours of collection. Upon arrival, samples were immediately prepared for analysis.

A total of 27 sediment, 4 soil, and 89 aquatic biota samples were analyzed for the 1972-73 period. In 1973-74, 10 soil and 23 aquatic biota samples were collected; other samples include 20 birds, 6 mice, 41 rats, and 22 mongooses. Table 1 lists all species collected.

### *Analytical Procedures*

The analytical method used for mirex residues was essentially the same as the method recommended by Wilson (*1*). In the present study the method was applied to certain types of biological species not heretofore examined by this procedure.

Equipment included a Waring blendor; a Sorvall Omnimixer; a Buchi rotary vacuum evaporator; a Soxhlet apparatus, size 23; 400-mm-by-20-mm-ID chromatographic columns with 200-ml reservoir fitted with teflon ultramax valves; and glass wool rinsed with acetone and hexane, air-dried, and heated at 200°C for 16 hours before use. All glassware was soaked in a sulfuric acid:

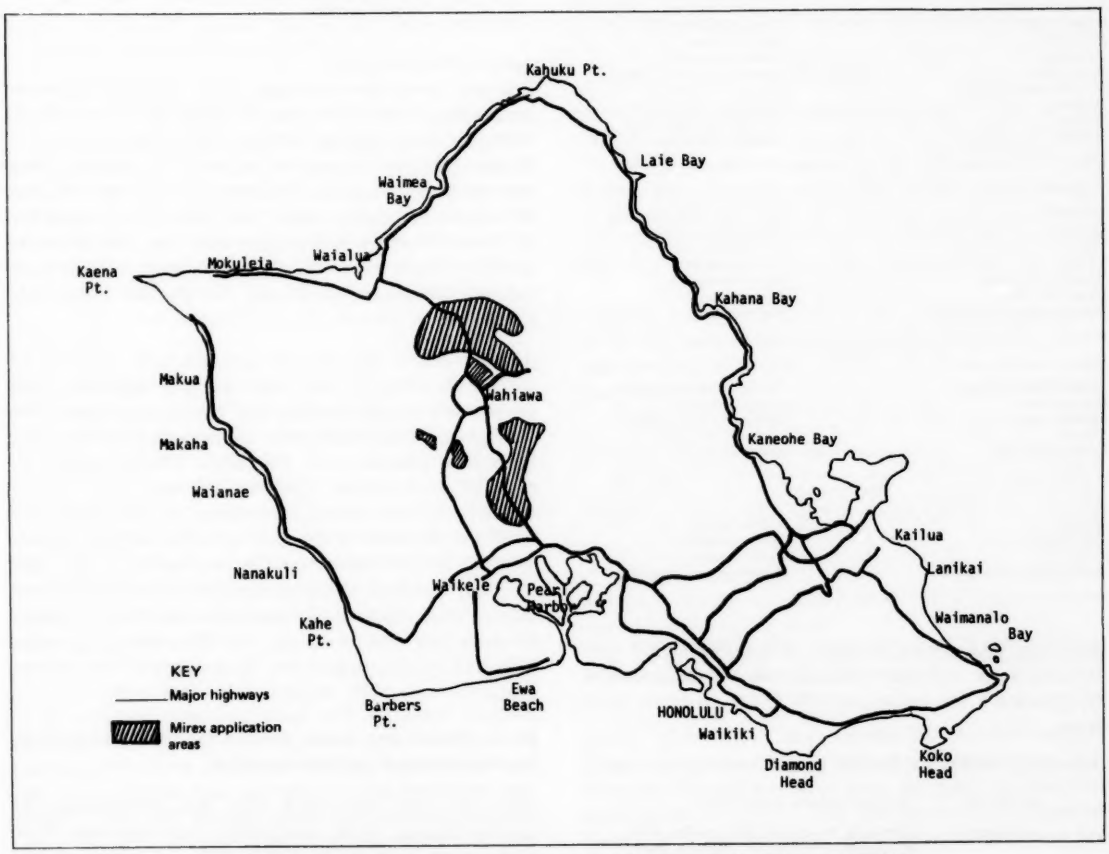


FIGURE 3. *Pineapple-growing areas treated with mirex, Oahu, Hawaii—1972-73*

TABLE 1. *Species sampled for mirex residues, Hawaiian pineapple-growing areas—1972-74*

| Common Name | Scientific Name |
|---|---|
| **Algae** | |
| | *Chnospora* sp. |
| | *Acanthophora specifera* |
| | *Sargassum* sp. |
| **Crustaceae** | |
| Crab | *Portunus sanguinolentus* |
| Crab | *Grapsus grapsus* |
| Crenate swimming crab | *Thalamita crenata* |
| Long-eyed swimming crab | *Podophthalmus vigil* |
| Shrimp | *Palaemon debilis* |
| **Echinoderm** | |
| Sea cucumber | *Holothuria atra* |
| Sea urchin | *Tripneustes gratilla* |
| Flat sea urchin | *Colobocentrotus atratus* |
| **Fish** | |
| Aholehole | *Kuhlia sandvicensis* |
| Great barracuda | *Sphraena barracuda* |
| Largemouth bass | *Micropterus salmoides* |
| Damselfish | *Abudefduf abdominalis* |
| Goatfish | *Parupeneus multifasciatus* |
| Goatfish | *Parupeneus porphyreus* |
| Halibut | *Bothus pantherinus* |
| Mollie | *Mollienisia latipinna* |
| Striped mullet | *Mugil cephalus* |
| False mullet | *Neomyxus chaptalii* |
| Parrotfish | *Scarus dubius* |
| Pompano | *Caranx ignobilis* |
| Surgeonfish | *Acanthurus candvicensis* |
| Mozambique tilapia | *Tilapia mossambica* |
| Wrasse | *Anampses godeffroyi* |
| Wrasse | *Thalassoma duperreyi* |
| Wrasse | *Thalassoma fuscum* |
| **Mollusk** | |
| Clam | *Quadrans palatam* |
| Mussel | *Isognomon californicum* |
| Oyster | *Crassostrea virginica* |
| Limpet | *Cellana calcosa* |
| Limpet | *Cellana exerata* |
| Rough periwinkle | *Littorina scabra* |
| Open dye shell | *Purpura aperta* |
| Nerita (pitchy sea snail) | *Nerita picea* |
| **Birds** | |
| Golden Pacific plover | *Pluvialis dominica fulva* |
| Barred dove | *Geopelia striata* |
| Spotted dove | *Streptopelia chinensis* |
| Mynah | *Acridotheres tristis* |
| Ruddy turnstone | *Arenaria interpres* |
| **Mammals** | |
| Mouse | *Mus musculus* |
| Polynesian rat | *Rattus exulans* |
| Roof rat | *Rattus rattus* |
| Small Indian mongoose | *Herpestus auropunctatus* |

potassium dichromate solution, rinsed thoroughly with distilled water and then with acetone and hexane. The dry glassware was heated at 200°C for 16 hours prior to use.

Operating conditions for the gas chromatograph were:

| | |
|---|---|
| Instrument: | Hewlett-Packard model 5750 |
| Columns: | Glass, ¼ in. by 4 ft OD, packed with 2 percent OV-101 on 100/120 mesh Gas Chrom Q |
| For confirmation: | Glass, ¼ in. by 4 ft OD, packed with 0.75 percent OV-17 and 0.97 percent OV-210 on 100/120 mesh Gas Chrom Q |
| Detector: | Electron-capture, with 200 mCi tritium as ionizing source |
| Temperatures: | Column 196°C<br>Injector 212°C<br>Detector 207°C |
| Carrier Gas: | Argon:methane (90:10) flowing at 60 ml/min |

The following reagents were employed:

Sodium sulfate: anhydrous powder, J. T. Baker No. 3898

QUSO-G30: precipitated silica (Philadelphia Quartz Co., Philadelphia, Pa.)

Desiccant mix: 10 percent QUSO, 90 percent anhydrous sodium sulfate

Acetone, acetonitrile, hexane, petroleum ether: all redistilled

Ethyl ether: Mallinckrodt No. 0844

Florisil: Regular grade (Floridin Co., Berkeley Springs, W. Va.), heated 5 hours at 130°C

Eluting solvents

A: 100 ml distilled water made to 1000 ml volume with acetonitrile

B: 60 ml ethyl ether made to 1000 ml volume with petroleum ether

## SAMPLE PREPARATION

*Soil and Sediments:* Samples were air-dried at room temperature, 20°-25°C, for 72 hours, then mixed for 1 minute in a Waring blendor and stored in pint-size Mason jars for subsequent analysis. A separate 10-g portion of each soil or sediment sample was weighed in a tared aluminum dish. The sample was dried for 16 hours at room temperature and then for 16 hours at 110°C in an air oven. After cooling in a desiccator, samples were reweighed and the percent solids was calculated.

*Aquatic Biota:* Initially, all samples were blotted dry and weighed. Shells were removed and discarded from all mollusk samples except the Nerita specimens. The operculum of the snails and the carapace of the crabs were also removed and discarded. The remainder of each of these species was homogenized in a Waring blendor. Sea cucumbers, sea urchins, shrimp, algae, and small fish less than 4 cm were prepared for whole-body analysis by homogenization in a blendor. Larger fish weighing less than 150 g were scaled; the head, tail, and viscera were removed and discarded; and the remainder of each fish was homogenized. Fish weighing more than 150 g were scaled and fillet samples were homogenized.

*Birds:* Breast and wing muscles of the dressed birds were composited and homogenized.

*Mice and Rats:* The head, feet, skin, and viscera, including kidney, heart, and lungs, were removed from each specimen and discarded. The remainder of the

mice was homogenized for analysis. Samples of tissue were removed from the back and legs of the rats and homogenized for analysis.

*Mongooses:* Samples of tissue from the two hind legs and lower back were removed from each skinned mongoose and homogenized for analysis. A 30-g sample of each homogenized specimen was weighed into a pint-size Mason jar and chilled at −10°C for 30 minutes. A quantity of the desiccant mix was added to the chilled sample and mixed thoroughly with a spatula. The amount of desiccant mix added to each sample varied from two to four times the weight of the specimen and was governed by the wetness of the sample. The mixture was frozen and then pulverized in a Sorvall Omni-mixer. It was necessary to refreeze and regrind the samples several times to obtain a free-flowing powdery mixture. Prepared samples were stored in the freezer until analysis.

### SAMPLE EXTRACTION

The biota sample was packed between two 1-inch layers of glass wool and Soxhlet-extracted for 4 hours with petroleum ether at a solvent cycle rate of 6-7 minutes. The extraction procedure for sediment and soil was similar except that the extract mixture was composed of acetone : petroleum ether (1:9).

### SAMPLE CLEANUP

Extracts were concentrated to approximately 10 ml in a rotary evaporator. The biota concentrates were transferred with petroleum ether in 3-4-ml portions to chromatographic columns containing 3 inches of unheated florisil. A gentle vacuum was applied to the columns after the addition of each portion to evaporate the solvent from the column. Residues were then eluted from the columns with 70 ml eluting solvent A and the eluate was evaporated to dryness in a rotary evaporator.

Biota residues obtained from this cleanup procedure were dissolved in petroleum ether and the sediment and soil concentrated extracts were transferred to chromatographic columns containing 4 inches of heat-treated florisil and topped with ½ inch anhydrous sodium sulfate. Columns had been previously washed with petroleum ether. Residues were eluted from the columns with 200 ml eluting solvent B. Eluates were evaporated to approximately 1 ml in a rotary evaporator, transferred to volumetric flasks, and made to volume with hexane. Suitable aliquots of the sample extracts and standardized solutions of mirex were applied to the gas chromatograph. Peak heights were compared and mirex residues were calculated and recorded. Samples of sediment, soil, and aquatic and terrestrial biota were fortified with mirex at the 0.1-0.5 ppm level to substantiate the efficiency and reliability of the analytical procedure (Table 2). Residue data reported have not been corrected for recovery. Analytical specificity was confirmed by examination of mirex residues found in mongooses and rats by mass spectrometry/gas chromatography with the utilization of a Finnigan Model 3000 GC Quadropole Mass Spectrometer Peak Identifier.

TABLE 2. *Percent recovery of mirex from soils and biota, Hawaiian pineapple-growing areas—1972-74* [1]

| SAMPLE | PERCENT RECOVERY |
|---|---|
| Sediment | 96 |
| | 91 |
| | 75 |
| | 87 |
| | 94 |
| Soil | 80 |
| | 91 |
| Barracuda | 90 |
| Goatfish | 86 |
| Mollie | 90 |
| Wrasse | 98 |
| Crenate crab | 94 |
| | 90 |
| Limpet | 98 |
| | 92 |
| | 91 |
| Nerita | 76 |
| Sea cucumber | 96 |
| Sea urchin | 92 |
| Flat sea urchin | 93 |
| Rat | 77 |

[1] All samples were spiked with 0.1 ppm mirex except the Nerita which received 0.5 ppm.

## *Results*

Mirex bait is aerially applied once each year at the rate of 2.5 lb (1,134 g)/acre in the pineapple fields. The active insecticide ingredient in this amount is 3.29 g. To comprehend the significance of this small amount of insecticide per acre in terms of potential environmental contamination, several physical properties of the bait were measured in the laboratory (Table 3).

TABLE 3. *Properties of mirex bait formulation applied, Hawaiian pineapple-growing areas—1972-74*

| | |
|---|---|
| Mirex content, % | 0.29 |
| Average mass of individual bait grains, mg | 0.783 |
| Range | 0.1-3.0 |
| Settling rate of bait grains in water, cm/sec [1] | |
| Majority of grains | 5.9 |
| Fastest rate | 11.8 |
| Solubility of mirex in water at 25°C: 3 trials, ppm [2] | 0.048 |
| | 0.093 |
| | 0.073 |
| Average solubility, ppm | 0.071 |

[1] Less than 1% of the bait floats.
[2] One bait was agitated gently in tap water for 2 hr, then allowed to soak overnight or 22 hr. The filtrate, passed through Whatman No. 42 analytical grade paper, was analyzed for mirex.

Only 5 fish and 3 soil samples of the 120 samples collected for the 1972-73 season contained mirex residues and all residues were near the level of analytical detectability (Table 4). The five fish samples originated from the Maui estuaries. The limit of detection for mirex ranged from 3 to 6 ppb. Fish species similar to

TABLE 4. *Mirex residues in environmental samples, Hawaiian pineapple-growing areas—1972-74*

| SPECIMEN [1] | COLLECTION SITE | MIREX RESIDUE, µG/KG |
|---|---|---|
| Goatfish (1) | Maliko Bay, Maui | 3 |
| Wrasse (1) | Maliko Bay, Maui | 3 |
| Aholehole (1) | Honokohau Bay, Maui | 3 |
| Aholehole (2) | Maliko Bay, Maui | 4 |
| Aholehole (18) | Honokohau Bay, Maui | 7 |
| Soil [2] | Palaau Field, Molokai | |
| | September 8, 1972 | ND |
| | December 8, 1972 | 18 |
| | March 15, 1973 | 10 |
| | June 15, 1973 | 15 |
| Control Series, Fish [3] | | |
| Goatfish (2) | Makua, Oahu | ND |
| Goatfish (2) | Kaneohe Bay, Oahu | ND |
| Aholehole (1) | Kaneohe Bay, Oahu | ND |

NOTE: ND = not detected.

[1] Number in parentheses indicates number of samples; residues in fish reported on fresh-tissue basis.
[2] Soil sampled from edge of field treated with mirex October 30, 1972; residues reported on air-dried basis.
[3] Specimens obtained in areas remote from mirex usage.

the specimens which contained residues were obtained far from mirex usage areas and were analyzed for mirex residue to make certain that the residue observed in the fish had indeed been contributed by mirex and not by an inherent gas-chromatographic-sensitive component characteristic of these species. These samples did not positively show mirex residues. It is possible for a fish to have randomly ingested one bait particle which would contribute a residue in the fish and it would be commensurate with the amounts of mirex in Table 3. Analytical residue results for the first season's monitoring program did not indicate any environmental problem resulting from the use of mirex in the pineapple fields, at least not in terms of aquatic biota and sediment contamination. However, the random finding of very low amounts of residue in the aforementioned fish and the apparent small but persistent residue found in the soil of one field (Table 4) prompted a second sample collection which was confined to the island of Maui and included a terrestrial vertebrate sampling program.

EPA permitted aerial application of mirex to the Hawaiian pineapple fields during the 1973-74 season provided that a monitoring program be continued as set forth in the Agency's Determination and Order dated August 31, 1973.

In the second season, top soil samples were obtained from two treated fields at a point where surface runoff would converge after leaving the fields. Areas from which the samples were taken consisted of well-drained soils with gentle to moderate slopes. Two samples from field No. 233 obtained within 3 months after mirex application contained 3-4 ppb mirex. Samples obtained from the same field 6-8 months later contained no detectable mirex residues. Samples obtained from field No. 234 during the same period of time contained mirex residues in the range of 5-9 ppb (Table 5).

TABLE 5. *Mirex residues in soil and fish samples, Hawaiian pineapple-growing areas—1973-74*

| SAMPLE [1, 2] | DATE | MIREX RESIDUE, µG/KG |
|---|---|---|
| Soil, Maui field 233 | October 6, 1973 [3] | ND |
| | November 3, 1973 | 3 |
| | January 19, 1974 | 4 |
| | April 21, 1974 | ND |
| | July 13, 1974 | ND |
| Soil, Maui field 234 | October 6, 1973 | ND |
| | November 2, 1973 | 9 |
| | January 19, 1974 | 5 |
| | April 21, 1974 | 9 |
| | July 13, 1974 | 9 |
| Fish | | |
| Wrasse (1) | October 6, 1973 | 3 |
| Aholehole (1) | October 6, 1973 | 3 |
| Aholehole (1) | April 21, 1974 | 3 |

NOTE: ND = not detected.

[1] Soil samples taken adjacent to fields where surface runoff converged after exiting the field. Soil residues reported on dry-weight basis.
[2] Analyses of only 3 fish of 23 aquatic biota indicated the presence of a low level of mirex residue. Number in parentheses indicates number of samples; residues in fish reported on fresh-tissue basis.
[3] October 6, 1973, was 1 week before mirex application.

A total of 11 marine fish, 5 mollusk, 3 echinoderm, and 2 seaweed samples were collected from the Maliko and Honokohau areas. Only three of the marine fish contained mirex residues (Table 5); each residue was at the minimum detectable level. Freshwater fauna sampled near the end of the second collection to determine whether mirex was accumulating in this area of the local environment contained no mirex residues.

## *Discussion*

Markin et al. (*2*) published data from an island near Gulfport, Miss., which had been treated with mirex three times in 1 year. Residues appeared in practically all marine life examined in the area 3 weeks after the third mirex treatment. Residues decreased to either undetectable or trace amounts in the subsequent 3-year period. Bretcke et al. (*3*) found residues in most of the fish examined in certain areas of Mississippi where mirex had been used extensively for at least 5 years before the sampling program. Borthwick et al. (*4*) examined estuarine wildlife in an area of South Carolina 24 months after treatment of the area with mirex and found residues greater than 0.01 ppm in only 10 percent of the specimens examined.

In a study of a crawfish-growing area of Louisiana Markin et al. (*5*) found, in most instances, no mirex residues in crawfish, some of which had been obtained from areas treated five times during the year prior to the sampling program. The absence of mirex residues in the aquatic areas of Hawaii may be attributed to

several factors: in some areas reservoirs and irrigation canals receive all runoff water because there are no large rivers or streams in the pineapple-producing areas of the State; normal rainfall is quickly absorbed by the volcanic soils; and soil and water conservation measures, including contour plowing, diking, and grassing of water courses, are constantly practiced to contain the soil and water within the pineapple fields so that runoff is limited to roadways and newly planted fields.

Bird samples were predominantly from golden Pacific plover. This bird and the ruddy turnstone are migratory and reside in Hawaii from September to May. Both species feed principally on insects and larvae, preferably in newly plowed and planted fields. Mirex residues in plovers varied considerably between samples from 80 to 10,400 ppb (Table 6); no definitive cumulative or diminutive trend of residues with time was apparent. It is reasonable to assume that the plover which weighed 127 g and contained 10.4 ppm mirex in its body tissue could have randomly acquired these residues from less than 0.5 g bait (Table 3) or from insects which had ingested the bait (*2*). Yet plover data (Table 6) indicate that these levels were exceptionally high. Furthermore, bait deteriorates rapidly in the field, becoming unacceptable to the birds as a feedstuff. Similarly, residue data obtained from a limited number of samples of the ruddy turnstone and the mynah were inconclusive.

Difficulty in acquiring definite time-related data on a migratory species over a period of 7 months is readily apparent in the data in Table 6. Except for one specimen which had a trace of mirex, less than 10 ppb, no residues were found in the doves.

Oberheu (*6*) examined starlings, which are also migratory birds. Samples were obtained from mirex-treated areas of seven southeastern States. Oberheu concluded that mirex residues found in the birds (80-1,666 ppb) related directly to the exposure potential but admitted that the significance of the levels was not explainable. Ivie et al. (*7*) noted that mirex residue levels in birds varied appreciably in different species. Their controlled study with mirex-treated quail indicated that mirex was

TABLE 6. *Mirex residues in birds, Hawaiian pineapple-growing areas—1973-74*

| Date | Mirex Residue, μg/kg | | | | |
|---|---|---|---|---|---|
| | Barred Dove | Lace-Necked Dove | Mynah | Golden Pacific Plover | Ruddy Turnstone |
| October 11, 1973 [1] | 6 (1) | | | 118 (2) | |
| October 31, 1973 | | | | 1,955 (4) | |
| November 20, 1973 | | | | 440 (1) | 210 (1) |
| November 20, 1973 | | | | 310 (1) | |
| January 17, 1974 | ND (1) | | 325 (1) | 625 (1) | 810 (1) |
| February 27, 1974 | | | 30 (1) | 10,400 (1) | |
| " " " | | | | 1,250 (1) | |
| " " " | | | | 180 (1) | |
| " " " | | | | 330 (1) | |
| April 17,1974 | | | | 80 (1) | 200 (1) |
| July 10, 1974 | | ND (1) | | | |

NOTE: ND = not detected.

[1] October 11, 1973, was 1 week before seasonal mirex application. Number in parentheses indicates number of samples; residues in birds reported on fresh whole-tissue basis.

TABLE 7. *Mirex residues in mice and rats, Hawaiian pineapple-growing areas—1973-74*

| Date | Weeks after Application | Mirex residues, μg/kg | | | | |
|---|---|---|---|---|---|---|
| | | Mouse | Polynesian Rat | Geometric Mean | Roof Rat | Geometric Mean |
| 10-11-73 [1] | | 281 (4) | 67 (5) | | 13 (4) | |
| 11-01-73 | 3 | 379 (1) | 8,435 (5) | | 1,060 (5) | |
| 11-21-73 | 6 | | 1,570 (1) | | 1,850 (1) | |
| | | | 890 (1) | | 110 (1) | |
| | | | 1,470 (1) | 1,270 | 770 (1) | 666 |
| | | | 1,280 (1) | | 500 (1) | |
| | | | | | 1,670 (1) | |
| 01-17-74 | 14 | 890 (1) | 9,410 (1) | | 295 (1) | |
| | | | 790 (1) | | 925 (1) | |
| | | | 125 (1) | 976 | 830 (1) | 683 |
| | | | | | 960 (1) | |
| 02-28-74 | 20 | | 350 (1) | 388 | 95 (1) | 149 |
| | | | 430 (1) | | 235 (1) | |
| 04-17-74 | 27 | | 890 (1) | | 120 (1) | |
| | | | 50 (1) | | 85 (1) | |
| | | | 150 (1) | 188 | 135 (1) | 212 |
| | | | | | 715 (1) | |
| | | | | | 435 (1) | |
| 07-10-74 | 39 | | 133 (1) | | 13 (1) | |
| | | | 47 (1) | | 5 (1) | |
| | | | 68 (1) | 56 | 24 (1) | 17 |
| | | | 24 (1) | | 21 (1) | |
| | | | | | 49 (1) | |

NOTE: Number in parentheses indicates number of samples; residues in specimens reported on fresh whole-tissue basis.

[1] October 11, 1973, was 1 week before seasonal mirex application.

rapidly absorbed by body fat, particularly in males. Residue levels in female quail declined rapidly because the residue was transferred to the eggs. Residues in the male declined more slowly; 50 percent of the administered mirex was still present in the male tissue 84 days after treatment. Markin et al. (*2*) reported residues of mirex in sandpipers and snowy egrets in the range of 440-1,320 ppb 1 year after the last of three mirex applications. Residues decreased to about 35 ppb in both species 2 years later. However, authors of that study observed no effect on the overall population of the area.

All samples of mice and rats were obtained from the same pineapple field. The Polynesian rat, which is limited to a diametral feeding range of about 100 feet, feeds on pineapple stumps, arthropods, and seeds. The roof rat has a feeding range of about 200 feet; its indiscriminate food selection includes grass, fruits, birds, and bird eggs.

Mirex residues in mice samples (Table 7) ranged from 281 to 890 ppb; data were insufficient to indicate a trend in accumulation or excretion. Residues in the Polynesian rat ranged from 24 to 9,410 ppb. (Table 7). Levels dropped markedly after the 13th week after mirex application. Residues in the roof rat ranged from 5 to 1,850 ppb and, similarly, residue levels decreased with time.

Gibson et al. (*8*) and Mehendale et al. (*9*) noted differences in excretion patterns after feeding mirex to laboratory-controlled rats. Gibson's group noted that 18 percent of the mirex was eliminated from rats within a 7-day period, whereas Mehendale et al. reported that about 59 percent was eliminated during the same time period. Both groups noted that the remainder of the pesticide would be eliminated slowly from the body tissue of the rats. Obviously, controlled laboratory studies cannot be readily or easily correlated to the rodent living in the wild.

The small Indian mongoose was included in the sampling program because it represented the highest trophic level of the food chain in the pineapple fields. The only true carnivore that frequents the fields, the Hawaiian or Pueo owl, may be classed as an endangered species; thus specimens were not taken, nor were any observed during the program. The mongoose eats birds, small mammals, plant material, detritus, garbage, or any other organic material available. They have a feeding range of about one-fourth mile. The 22 mongooses trapped in field No. 235 had mirex residues ranging from 30 to 11,760 ppb (Table 8). Mongooses trapped about 1 mile from the treated area (Table 8) contained average mirex residues of 126 ppb, somewhat lower than the average value of the samples obtained in the treated area on the same sampling date.

These latter data may be misleading. If the one high residue value of 1,250 ppb from field No. 235 on April 16, 1974, were excluded, the average mirex residues in the mongoose from the two areas would be 114 ppb and 126 ppb, respectively, indicating no tangible difference in the values for the two areas. However, residue concentrations in the mongoose species did decrease with time. This was markedly apparent 27-39 weeks after mirex application. An examination of six mongoose fetuses and the respective mothers indicated that mirex residues in the fetuses were about 14 percent of the amount found in the mothers (Table 9).

TABLE 8. *Mirex residues in small Indian mongoose, Hawaiian pineapple-growing areas—1973-74*

| Date | Weeks after Application | Collection Site | Residue, µg/kg | Geometric Mean, ppb |
|---|---|---|---|---|
| 11-21-73 [1] | 6 | Field 235 | 430 | |
| | | | 6,190 | |
| | | | 3,930 | |
| | | | 9,820 | |
| | | | 500 | 2,200 |
| 01-17-74 | 14 | Field 235 | 11,760 | |
| | | | 2,080 | |
| | | | 6,665 | 5,460 |
| 02-27-74 | 20 | Field 235 | 2,940 | |
| | | | 4,120 | |
| | | | 1,730 | |
| | | | 470 | 1,770 |
| 04-16-74 | 27 | Field 235 | 1,250 | |
| | | | 30 | |
| | | | 70 | |
| | | | 305 | |
| | | | 50 | 132 |
| 07-10-74 | 39 | Field 235 | 576 | |
| | | | 200 | |
| | | | 533 | |
| | | | 333 | |
| | | | 37 | 238 |
| 04-16-74 | 27 | 1 mile seaward from fields 233-234 | 35 | |
| | | | 370 | |
| | | | 90 | |
| | | | 105 | |
| | | | 30 | 82 |

NOTE: Each of above residue values represents the residue in one mongoose specimen; residues reported on fresh whole-tissue basis.

[1] Mirex had been applied to the field during the week of October 19, 1973.

TABLE 9. *Comparison of mirex residues in the fetus and related mother of small Indian mongooses, Hawaiian pineapple-growing area—1972-74*

| Collection Site | Residue, µg/kg | | |
|---|---|---|---|
| | Mother | Fetus | Fetus/Mother |
| Edge of mirex-treated field No. 235 | 4,120 | 625 | 0.15 |
| 1 mile from mirex-treated field No. 233, 234 | 350 | 15 | 0.04 |
| " | 145 | 20 | 0.14 |
| " | 20 | 6 | 0.30 |
| " | 480 | 60 | 0.13 |

NOTE: Samples obtained February 27, 1974, about 4.5 months after mirex application. Each residue value represents the residue in one mongoose specimen except for the fetus value of 625, which was obtained from a composite sample of two fetuses. Residues reported on fresh whole-tissue basis.

In summation, aerial application of mirex to the pineapple fields did not contaminate the Hawaiian marine environment. During the monitoring period of 1972-74, only 8 fish of 112 aquatic biota samples contained mirex residues, and these 8 samples contained only negligible amounts less than 10 ppb. No evidence of food web pesticide residue accumulation was apparent in the local aquatic biota. Mirex residue levels in pineapple field soils were very low (3-18 ppb) but persistent for the 6- to 9-month period after mirex application. Residue levels in the mongoose, the highest member of the food web examined from the pineapple fields, were at a maximum amount 6-14 weeks after mirex application. A marked drop in residue levels in this species was observed in the subsequent time period, 27-40 weeks after mirex application. A similar trend was observed in the rats. Data indicated that mirex accumulation in terrestrial biota of the mirex-treated pineapple fields was temporary and no permanent buildup or food web accumulation of residue was evident, with the possible exception of the Pacific golden plover.


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# *Exposure and Contamination of the Air and Employees of a Pentachlorophenol Plant, Idaho—1972* [1,2]

Joseph A. Wyllie, Joe Gabica, W. W. Benson, and Julie Yoder


## ABSTRACT

*A pentachlorophenol (PCP) wood treatment plant was studied to determine PCP exposure to people by occupation and to the plant by work area. This plant operates on a year-round basis with a 25 percent increase in production from May through October. Approximately 2.5 million board feet of timber are processed annually. Samples were taken in the morning of the second work week of each month for 5 consecutive months. Samples consisted of serum and urine from the employees and air from locations throughout the plant work area. All samples were analyzed for PCP residue. Peripheral blood was used to culture cells to investigate possible chromosomal aberrations.*


## *Introduction*

Pentachlorophenol (PCP) has been used to treat wood products for preservation and control of insects and fungus since the late 1930's (*1-4*).

A study of a small wood treatment plant and its six full-time employees was conducted to determine their exposure by air and environmental contact to PCP and how this exposure possibly affected chromosomes.

## *Sampling and Analysis*

Blood and urine samples were collected monthly from January through May. The ages of the employees ranged from 20 to 54 years. Employee work stations and their length of employment and/or exposure are shown in Table 1. The main tasks of the employees are listed, but as is typical in a plant of this size, all are trained in each capacity and often function accordingly. Respirators and rubber gloves are worn when working inside the treatment chamber and while mixing concentrates. Other than at these times, no protective gear is worn.

The method of analysis for serum and urine was that of Rivers (*5*). Two ml serum or urine was added to a culture tube along with 6 ml benzene and two drops of concentrated sulfuric acid. The tube and contents were then rotated for 2 hours at 50 rpm on a roto-rack. Three ml of the benzene was transferred to a centrifuge tube and methylated with 0.2 ml diazomethane. The sample was then ready for dilution and gas chromatography. Recovery data were collected by running samples in duplicate spike at 0.1, 0.5, 5, and 50 ppm (Table 2). Reagent blanks were run with each set of samples.

Air samples were taken from the 11 sites shown in Figure 1. A series of three MSA Monitaire midget impingers were used to collect the first test samples, but after the first analysis two impingers were dropped because results showed all the PCP was trapped in the first impinger. Ten ml ethylene glycol was placed in each impinger. Air samples were collected for an average of 6 hours during the working day. Two ml ethylene glycol from each impinger was then extracted using the Rivers method for blood and urine.

Chromosome work was done using a slight modification of the technique of Difco Laboratories (*6*). Peripheral blood cultures were incubated at 38°C and samples were cultured for 48 hours to obtain cells in the first mitotic division (*7*). Slides were stained with Giemsa and rearranged and coded by a person other than the scorer to avoid bias. Twenty-five cells were scored as to chromosome number, abnormal configurations, breaks, and gaps. Photographs were taken of all abnormal bursts and karyotypes were done when there was evidence of loss of material. Gebhart's criteria were used to differentiate breaks and gaps from achromatic lesions (*8*). Gaps were considered abnormal because they vary in

[1] Idaho Epidemiologic Studies Project, Department of Health and Welfare, Statehouse, Boise, Idaho 83720.

[2] Research supported under Contract 68-02-0552 by the Pesticide Community Studies Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, through the Idaho Department of Health.

TABLE 1. *PCP residues in serum, whole blood, and urine of workers in a PCP plant and a control, Idaho—1972*

| Subject | Occupation | Age, Years | Exposure, Years | Residues, ppb | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | January | | February | | March | | April | | May | |
| | | | | Serum | Urine | Serum | Urine | Serum | Urine | Serum | Urine | Serum | Urine |
| 1 | Office Manager | 48 | 10 | 643.8 | 112.2 | 417.9 | 63.4 | 749.1 | 41.3 | 702.5 | 42.0 | 705.0 | 61.3 |
| 2 | Outside Loader | 29 | 2 | 372.9 | 132.5 | 348.4 | 111.1 | 610.0 | 124.6 | 1203.0 | 157.2 | 1630.0 | 151.2 |
| 3 | Welder and Laborer | 20 | 6 summers and 2 full years | 1236.0 | 245.5 | 1246.0 | 130.0 | 1580.0 | 80.9 | 1791.0 | 148.8 | 3963.0 | 262.3 |
| 4 | Pressure Treater | 54 | 5 | 1979.0 | 760.0 | 1508.0 | 121.8 | 1746.0 | 93.6 | 3550.0 | 188.6 | 2675.0 | 315.1 |
| 5 | Owner: Office and Yard | 47 | 11 | 1036.0 | 470.1 | 688.5 | 109.5 | 1110.0 | 107.2 | 1664.0 | 334.8 | 3001.0 | 179.5 |
| 6 | Outside Laborer | 44 | 2 | 540.0 | 151.1 | 405.7 | 44.4 | 737.5 | 56.3 | 2011.0 | 63.2 | 1321.0 | 53.0 |
| MEAN | | | | 967.9 | 312.0 | 769.1 | 96.7 | 1088.8 | 84.0 | 1820.2 | 155.8 | 2215.8 | 170.4 |
| 1 Control: Chemist | | | | 47.8 | 4.2 | 42.4 | 2.8 | 68.0 | 2.9 | 42.5 | 4.3 | 38.0 | 2.6 |

TABLE 2. *Recovery data, PCP analyses*

| Sample | Spiking Level, ng/g | Recovery of Duplicate Samples, % |
|---|---|---|
| Urine | .1 | 102 |
| | .5 | 107 |
| | 5.0 | 103 |
| | 50.0 | 99 |
| Serum | .1 | 98 |
| | .5 | 96 |
| | 5.0 | 93 |
| | 50.0 | 97 |
| Air | .1 | 93 |
| | .5 | 95 |
| | 5.0 | 100 |
| | 50.0 | 100 |

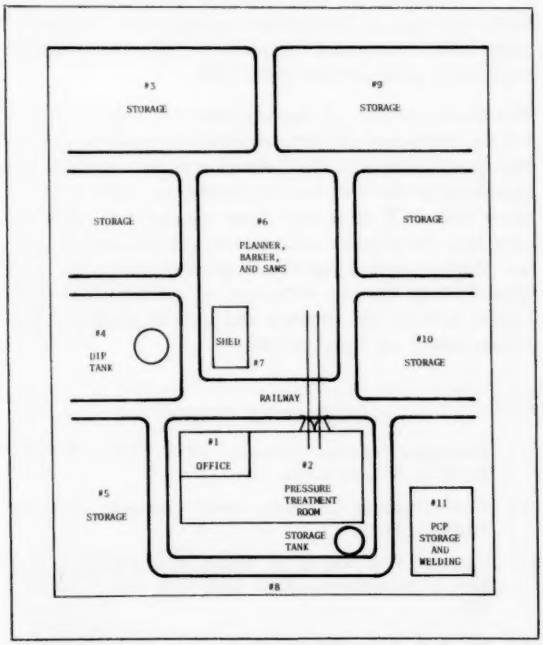


FIGURE 1. *Map of pentachlorophenol plant showing air sampling sites*

number due to the concentration and length of exposure (*8*). Six exposed and four control samples were used for the study. Background data on the control group of the cytogenetic study are listed in Table 3.

TABLE 3. *Background data on control group members of cytogenic studies*

| Subject | Sex | Age, years | Occupation | Exposure, years |
|---|---|---|---|---|
| 1X | M | 50 | Chemist | 30 |
| 2X | M | 31 | Chemist | 8 |
| 3X | M | 26 | Medical Technologist | 4 |
| 4X | M | 20 | Laboratory Technician | 2 |

All samples analyzed for PCP concentrations were injected into a Micro-Tek 220 gas chromatograph fitted with electron-capture detectors. Two columns were used, one as the working column and the other for confirmation. Parameters for the gas-liquid chromatography are listed below:

Columns: (A) Pyrex, u-shaped, 6 ft by ¼ in., packed with 100/120 mesh 4 percent SE-30/6 percent QF-1
(B) Pyrex, u-shaped, 6 ft by ¼ in., packed with 80/100 mesh 1.5 percent OV-17/1.95 percent QF-1

Temperatures:

| | |
|---|---|
| Oven | 200°C |
| Detector | 205°C |
| Inlet | 215°C |
| Transfer | 245°C |

Carrier Gas: Nitrogen

Flow Rate: 4 percent SE-30/6 percent QF-1: 100 ml/min
1.4 percent OV-17/1.95 percent QF-1: 70 ml/min

## *Results and Discussion*

Serum PCP levels (Table 2) of all subjects decreased during February and rose slightly in March and again in April with the exception of subject number 1, the office manager. Residue in his serum stayed at approxi-

mately the same level throughout the study. In May subjects 3, 5, and 2 had increased serum levels; those of subjects 4 and 6 returned to a lower level. This phenomenon cannot be explained by the investigator.

Serum PCP levels ranged from 348.4 to 3,963.0 ppb for the exposed group and from 38.0 to 68.0 ppb for the control group. The average levels for the exposed and control groups were 1,372.1 ppb and 47.7 ppb, respectively.

PCP levels in urine were quite a bit lower than those in serum (Table 2). Levels started at a high average (312 ppb) in January, plunged to a low (96.7 ppb) in February, stayed nearly the same in March (84.0 ppb), and then increased (155.8 ppb) in April. Levels in subjects 5, 6, and 2 dropped in May, although those of subjects 4, 3, and 1 continued to increase. Urine levels for the exposed group ranged from 41.3 to 760.6 ppb PCP. Levels in urine averaged 163.8 ppb for the exposed group and 3.4 ppb for the control group.

Results of the present study are comparable to those of urine analyses done by Cranmer and Freal in Florida. They analyzed six control urine samples in which PCP levels ranged from 2.2 to 10.8 ppb with a mean of 4.85 ppb. Levels in four urine samples from occupationally exposed individuals ranged from 24.1 to 265 ppb with a mean of 119.8 ppb PCP (*9*).

Bevenue et al. found PCP in urine in Hawaii. Levels ranged from 3 to 357,000 ppb with a mean value of 1,244 ppb for 211 samples of occupationally exposed individuals (*10*). They also reported on PCP in the urine of 290 individuals who were not exposed; levels ranged from 0 to 1,840 ppb with a mean of 40 ppb (*11*).

PCP residues in the urine of exposed workers studied by Bevenue et al. were 7.6 times higher than levels found in the urine of exposed workers in this study and 10.4 times higher than residues in the urine of exposed workers studied by Cranmer and Freal. Levels in the urine of the Hawaiian control group were 11.8 times higher than those of this study and 8.2 times higher than those taken in Florida. These discrepancies may be caused by the heavy use of PCP-treated products in Hawaii (*12, 13*) where PCP is used on wood products to control mold, mildew, and termites, on pineapple and in sugarcane fields (*10, 13*), and in many homes to control spot infestations of insects (*10*).

Air samples were collected during the middle of the work week on the same basis as the serum and urine samples (Table 4). Air samples 1 and 2 cannot be compared to the others because they were taken inside the pressure treatment building. Depending on which systems were working, levels would elevate and regress. Air sampling at all sites except 1 and 2 started in January. Levels were below 300 ng PCP/$m^3$ and dropped slightly in February. Residues at sites 7, 9, 10, and 11 increased in March to levels over 300 ng/$m^3$ while those at sites 3, 4, 5, and 6 stayed about the same. In April residues at all but two sites fell below 300 ng/$m^3$. In May levels rose at all stations except site 10. Residues at sites 1, 2, 6, and 11 rose dramatically to an average 3,546.9 ng/$m^3$ in May.

TABLE 4. *PCP residues in the air of a PCP plant, Idaho—1972*

| Site | Residues, ng/$m^3$ | | | | |
|---|---|---|---|---|---|
| | January | February | March | April | May |
| 1 | 1688.6 | 3189.8 | 571.1 | 187.9 | 3453.3 |
| 2 | 4854.2 | 15275.1 | 517.4 | 2206.8 | 7010.4 |
| 3 | 64.6 | 58.9 | 56.0 | 45.9 | 331.1 |
| 4 | 106.2 | 21.9 | 18.7 | 12.2 | 801.9 |
| 5 | 54.8 | 11.5 | 10.6 | 8.3 | 533.6 |
| 6 | 169.7 | 26.9 | 90.1 | 5.1 | 2581.5 |
| 7 | 61.9 | 30.1 | 561.4 | 42.9 | 739.7 |
| 8 | 87.3 | 79.7 | 86.5 | 87.5 | 1127.3 |
| 9 | 144.0 | 86.8 | 932.6 | 172.8 | 190.8 |
| 10 | 34.1 | 9.1 | 367.8 | 48.7 | 79.6 |
| 11 | 241.2 | 230.4 | 495.4 | 75.3 | 3917.6 |
| TOTAL | 7506.6 | 19020.2 | 3707.6 | 2893.4 | 20766.8 |
| AVERAGE | 682.4 | 1729.1 | 337.0 | 263.0 | 1887.9 |

Work done in Russia by Tabakova established a maximum permissible concentration of 40 ng/$m^3$ PCP in the air (*14*). Using this criterion as a maximum allowable limit, one can see that residues in the air of the general work areas throughout the plant are over the suggested tolerance a good portion of the time.

Statistical analyses of the exposed and control groups for the incidence of chromosomal aberrations (breaks and gaps) show that the difference in the means is not significant at the 0.05 level of confidence. This does not mean that PCP does not cause chromosome damage, only that the exposed and control groups studied were too small to permit significant generalizations and that there were no extreme differences in chromosomal aberrations between the exposed and control groups. Aberrations found are listed in Table 5.

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TABLE 5. *Chromosomal aberrations in workers in a PCP plant, Idaho—1972*

| Subject | January | | February | | March | | April | | May | |
|---|---|---|---|---|---|---|---|---|---|---|
| | No. Breaks | No. Gaps | No. Breaks | No. Gaps | No. Breaks | No. Gaps | No. Breaks | No. Gaps | No. Breaks | No. Gaps |
| **Exposed Group** | | | | | | | | | | |
| 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2 | 0 | 0 | 0 | 2 | 0 | 1 | 1 | 2 | 1 | 0 |
| 3 | 2 | 2 | 0 | 3 | 3 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0 | 1 | 0 | 1 | 0 | 2 | 0 | 1 | 0 | 1 |
| 5 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 3 |
| 6 | 0 | 0 | 3 | 0 | 1 | 3 | 0 | 0 | 0 | 0 |
| Subjects with aberrations, % | 17 | 33 | 33 | 83 | 17 | 66 | 17 | 33 | 17 | 33 |
| Average aberrations per 150 cells, % | 1.3 | 2.0 | 2.6 | 5.3 | 0.6 | 6.0 | 0.6 | 0.6 | 0.6 | 3.3 |
| **Control Group** | | | | | | | | | | |
| 1X | 0 | 1 | 0 | 1 | 0 | 2 | 0 | 1 | 0 | 2 |
| 2X | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 3X | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 |
| 4X | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 0 |
| Subjects with aberrations, % | 0 | 50 | 0 | 50 | 25 | 100 | 0 | 50 | 0 | 50 |
| Average aberrations per 150 cells, % | 0 | 2.0 | 0 | 2.0 | 0.1 | 5.0 | 0 | 2.0 | 0 | 3.0 |

# APPENDIX

## *Chemical Names of Compounds Discussed in This Issue*

| | |
|---|---|
| ALDRIN | Not less than 95% of 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene |
| ATRAZINE | 2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine |
| BHC (BENZENE HEXACHLORIDE) | 1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *gamma* is most active as an insecticide. |
| CHLORDANE | 1,2,3,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane. |
| CHLORPYRIFOS | *O,O*-Diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate |
| DDD | See TDE. |
| DDE | Dichlorodiphenyl dichloro-ethylene (degradation product of DDT)<br>*o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene<br>*p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene |
| DDT | Main component (*p,p'*-DDT): $\alpha$-Bis(*p*-chlorophenyl)$\beta,\beta,\beta$-trichloroethane<br>Other isomers are possible and some are present in the commercial product.<br>*o,p'*-DDT: 1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane |
| DIELDRIN | Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene |
| ENDRIN | 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene |
| HEPTACHLOR | 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene |
| HEPTACHLOR EPOXIDE | 1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane |
| LINDANE | *Gamma* isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity |
| MIREX | Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene |
| MONOCROTOPHOS | *Cis*-3-(dimethoxyphosphinyloxy)-*N*-methylcrotonamide |
| PCB'S (POLYCHLORINATED BIPHENYLS) | Mixtures of chlorinated byphenyl compounds having various percentages of chlorine |
| PCP | Pentachlorophenol |
| TDE | 2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane |

## *Information for Contributors*

The PESTICIDES MONITORING JOURNAL welcomes from all sources qualified data and interpretive information which contribute to the understanding and evaluation of pesticides and their residues in relation to man and his environment.

The publication is distributed principally to scientists and technicians associated with pesticide monitoring, research, and other programs concerned with the fate of pesticides following their application. Additional circulation is maintained for persons with related interests, notably those in the agricultural, chemical manufacturing, and food processing industries; medical and public health workers; and conservationists. Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Accuracy, reliability, and limitations of the sampling and analytical methods employed must be clearly demonstrated through the use of appropriate procedures, such as recovery experiments at appropriate levels, confirmatory tests, internal standards, and inter-laboratory checks. The procedure employed should be referenced or outlined in brief form, and crucial points or modifications should be noted. Check or control samples should be employed where possible, and the sensitivity of the method should be given, particularly when very low levels of pesticides are being reported. Specific note should be made regarding correction of data for percent recoveries.

——Preparation of manuscripts should be in conformance to the CBE STYLE MANUAL, 3d ed. Council of Biological Editors, Committee on Form and Style, American Institute of Biological Sciences, Washington, D. C., and/or the STYLE MANUAL of The United States Government Printing Office.

——An abstract (not to exceed 200 words) should accompany each manuscript submitted.

——All material should be submitted in duplicate (original and one carbon) and sent by first-class mail in flat form—not folded or rolled.

——Manuscripts should be typed on 8½ x 11 inch paper with generous margins on all sides, and each page should end with a completed paragraph.

——All copy, including tables and references, should be double spaced, and all pages should be numbered. The first page of the manuscript must contain authors' full names listed under the title, with affiliations, and addresses footnoted below.

——Charts, illustrations, and tables, properly titled, should be appended at the end of the article with a notation in text to show where they should be inserted.

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The Journal also welcomes "brief" papers reporting monitoring data of a preliminary nature or studies of limited scope. A section entitled *Briefs* will be included, as necessary, to provide space for papers of this type to present timely and informative data. These papers must be limited in length to two journal pages (850 words) and should conform to the format for regular papers accepted by the Journal.

Pesticides ordinarily should be identified by common or generic names approved by national scientific societies. The first reference to a particular pesticide should be followed by the chemical or scientific name in parentheses—assigned in accordance with CHEMICAL ABSTRACTS nomenclature. Structural chemical formulas should be used when appropriate. Published data and information require prior approval by the Editorial Advisory Board; however, endorsement of published information by any specific Federal agency is not intended or to be implied. Authors of accepted manuscripts will receive edited typescripts for approval before type is set. After publication, senior authors will be provided with 100 reprints.

Manuscripts are received and reviewed with the understanding that they previously have not been accepted for technical publication elsewhere. If a paper has been given or is intended for presentation at a meeting, or if a significant portion of its contents has been published or submitted for publication elsewhere, notations of such should be provided.

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